857. *The Potassium Thorium Fluorides.*

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Thermal analysis and microscopic examination have shown the following compounds to exist in the system KF–ThF_4 : α-K_5ThF_9, β-K_5ThF_9, K_3ThF_7, α-K_2ThF_6, β-K_2ThF_6, $KThF_5$, KTh_2F_9, and KTh_3F_{13}. The compound α-K_5ThF_9 has not previously been described. The compound K_3ThF_7 is stable only at high temperatures and has been shown to disproportionate at lower temperatures into a mixture of β-K_2ThF_6 and β-K_5ThF_9. Discordant views in the literature as to the formula of the compound of highest thorium fluoride content have been discussed, and the formula KTh_3F_{13} for this compound confirmed. Partial solid solution has been shown to occur between KTh_3F_{13} and ThF_4. Optical properties have been recorded for the majority of the compounds listed.

Systematic precipitation studies in the systems KF–$Th(NO_3)_4$–H_2O and KNO_3–$Th(NO_3)_4$–HF–H_2O have shown that cationic complexes of thorium and fluorine strongly influence the composition of the precipitated potassium thorium fluorides. The hydrated compounds α-K_2ThF_6,nH_2O, KTh_2F_9,nH_2O, and ThF_4,nH_2O have been isolated from solution, but the compound $KThF_5,nH_2O$ could not be isolated in a substantially pure state. Lattice water in the precipitated phases can be removed at 300° without appreciable loss of fluorine.

The preparation of hydrated potassium thorium fluorides approximating in composition to K_2ThF_6, $KThF_5$ (probably a mixture of K_2ThF_6 and KTh_2F_9), and KTh_2F_9 (Rosenheim, Samper and Davidsohn, *Z. anorg. Chem.*, 1903, **35**, 424) suggests a considerable degree of complexity for the binary system KF–ThF_4. Ample confirmation of this complexity was obtained from preliminary studies of the system and from the results of Dergunov and Bergman (*Doklady Acad. Nauk, S.S.R.*, 1948, **60**, 391) and Zachariasen (*J. Amer. Chem. Soc.*, 1948, **70**, 2147), published during the course of our investigations.

Dergunov and Bergman's thermal analysis suggested the existence, at least at high temperatures, of two compounds K_3ThF_7 and $KThF_5$ and indicated a formula KTh_3F_{13} for a congruently-melting compound appearing in the thorium-rich area of the system. No evidence was obtained for other compounds or for any polymorphic forms of the potassium thorium fluorides, nor was any evidence presented of solid solution between thorium fluoride and KTh_3F_{13}.

Zachariasen's *X*-ray examination, carried out on melts cooled to atmospheric temperature at different rates, revealed the existence of the compounds K_5ThF_9, α-K_2ThF_6, β-K_2ThF_6, $KThF_5$, and KTh_2F_9. The compound of highest ThF_4 : KF ratio was stated to be KTh_6F_{25}. No mention was made in this study of a compound of composition K_3ThF_7 or of any region of solid solution.

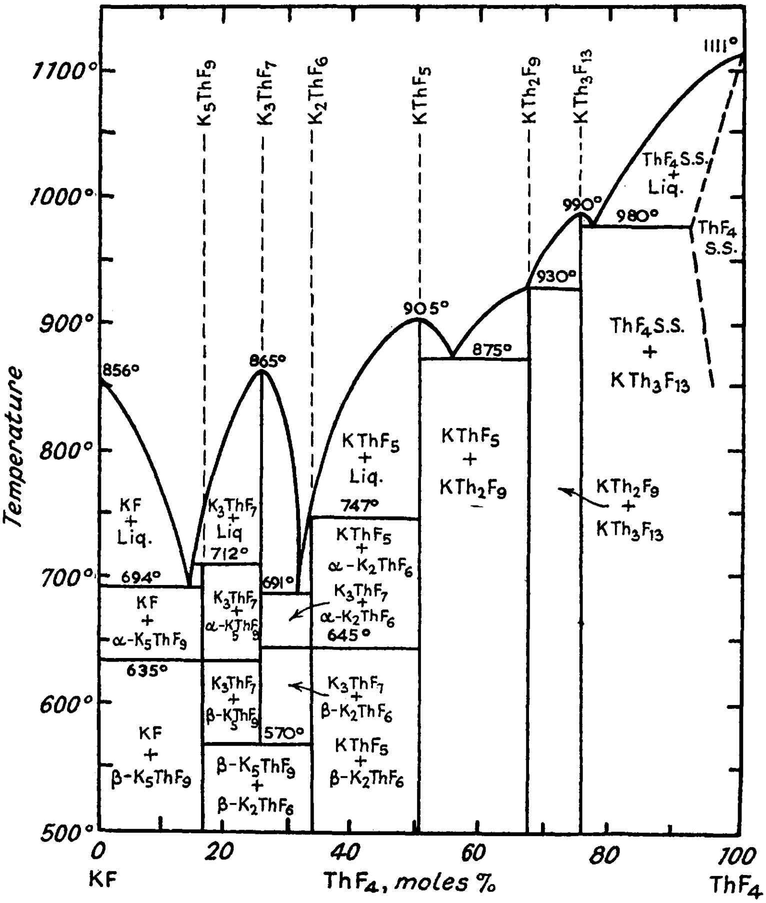
Since there are numerous discrepancies between the published results, a further study of the system KF–ThF_4 has been made by thermal analysis and by optical methods. Existence of an additional phase, α-K_5ThF_9, has been established. The compound K_3ThF_7 has been shown to disproportionate at approximately 570° into a mixture of β-K_5ThF_9 and β-K_2ThF_6. The composition of the phase in the thorium-rich portion of the system has been shown to be KTh_3F_{13}, rather than KTh_6F_{25}. This compound forms solid solutions with thorium fluoride containing up to 30% of KTh_3F_{13}. The only phases which could be precipitated in substantially pure state from aqueous solutions were hydrates of the compounds α-K_2ThF_6, KTh_2F_9, and ThF_4. Dehydration of these compounds without appreciable loss of fluorine could be completed by heating them for 3 hours at 300°, preferably in a current of inert gas.

Experimental

Materials.—Hydrofluoric acid, thorium nitrate, ammonium fluoride, potassium nitrate, and reagents used for analysis were of analytical grade. Potassium fluoride was of reagent grade.

Preparation of Anhydrous Fluorides.—Two methods of preparation of anhydrous thorium fluoride were used. (*a*) Thorium nitrate (M/2) was added at 20° to a 10% excess of 30% hydrofluoric acid. All fluoride solutions were handled in polystyrene equipment. After 15 hours, the precipitate changed from a voluminous gel to a dense powder. This was centrifuged and washed five times by redispersion in water to remove nitrate. The product was dehydrated by heating it for 3 hours at 300° (see p. 4475). (*b*) Thorium oxide was heated for 3 hours at 200° with a two-fold excess of ammonium fluoride, a ' Monel ' vessel attached to a trap and vacuum system being used. Excess of ammonium fluoride was removed, and ammonium thorium fluoride was finally decomposed by heating the product *in vacuo* ($<$0·05 mm.) for 1 hour at 430°. Progress of fluorination of thoria was followed by testing the solubility of the mixture in boiling 15% solutions of the tetrasodium salt of ethylenediaminetetra-acetic acid. Blank tests showed that this reagent did not dissolve unchanged thorium oxide. Products completely soluble in the reagent were obtained.

FIG. 1. *The system* KF–ThF_4.

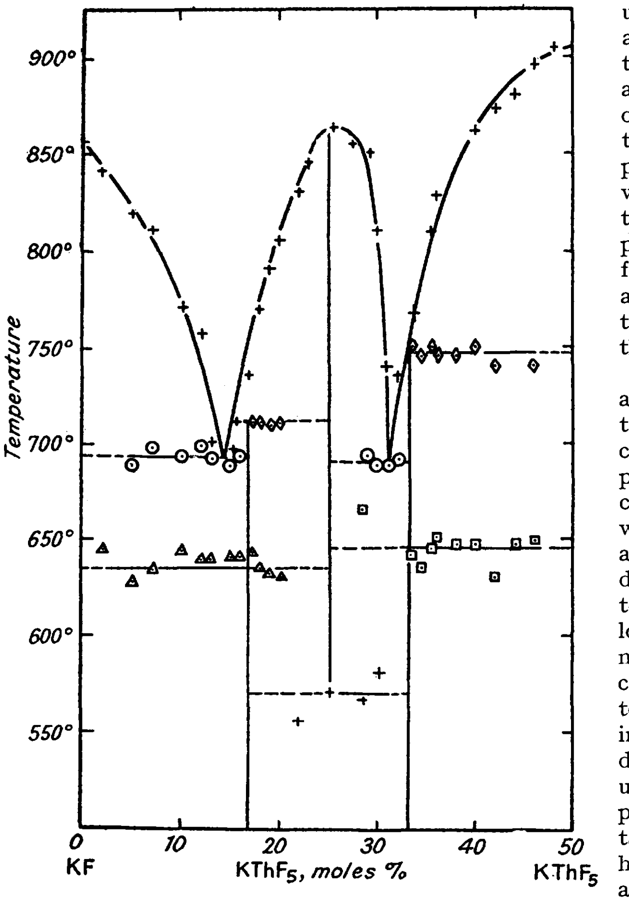


Traces of nitrate (0·005—0·01 mol.) and of ammonia (0·004—0·02 mol.) were detected in products made by methods (*a*) and (*b*), respectively. The atomic ratio of fluorine to thorium in precipitated thorium fluoride agreed with the theoretical value but fell to 3·96—3·97 after dehydration of the fluoride at 300°. Unless dehydration was complete, a further small loss of fluorine occurred on fusion of the product in argon. Since the bulk of the thorium fluoride used in the study of the system $KThF_5$–ThF_4 was prepared by this method, it was assumed that the product contained approximately 1% of oxyfluoride or oxide impurities, although neither of these compounds of high refractive index could be detected under the microscope. The effect of this quantity of oxyfluoride or oxide impurity on the m. p. of pure thorium fluoride was not investigated, but the effect was presumed to be small and to vanish at the composition $KThF_5$. Later work on thorium fluoride, including the determination of its m. p., was carried out with material made by method (*b*). The atomic ratio of fluorine to thorium in this product agreed with the theoretical value and was not changed by fusion of the product in argon.

A double fluoride served as a convenient source of material for work in the system KF–$KThF_5$. It was prepared by adding M-potassium fluoride (5 mol.) to 0·2M-thorium nitrate (1 mol.) and treating the precipitate as described for thorium fluoride. The composition of the product, after drying at 300°, was $K_{1\cdot05}ThF_{5\cdot04}$. Loss of fluorine from this product on drying or fusion was negligible.

Phase Analysis of the System KF–ThF_4.—(a) *Thermal analysis.* To maintain an atmosphere of argon over the charge, a crucible drilled from a length of " Monel " metal rod was placed in a vertical, close-fitting " Monel " tube which was sealed at its lower end. The upper end of this tube accommodated a " Sindanyo " plug with orifices for thermocouple leads, " Monel " stirrer, and argon supply. The major portion of the tube was heated in a well-lagged, tubular resistance furnace. The temperature of the charge was measured with a platinum–platinum-rhodium thermocouple and a thermocouple potentiometer. The thermocouple was frequently calibrated at the silver, zinc, and sodium chloride points, and at no time was found to be in error by more than +3° or −2°.

Fig. 2. *The system* KF–$KThF_5$.



All melts were stirred while cooling and the solidified products were used to obtain heating curves. With cooling curves, temperatures at the m. p.s of pure compounds, eutectics, and incongruent m. p.s were reproducible to within ±3°, but transition temperatures of solid compounds were reproducible to within only ±5°. Liquidus temperatures were often difficult to locate precisely and in general could not be easily reproduced. Heating curves enabled us to obtain eutectic temperatures and incongruent m. p.s in excellent agreement with those derived from cooling curves, but were unsatisfactory for locating liquidus points. Transition temperatures obtained from heating curves were higher than corresponding temperatures obtained from cooling curves by 10—20° for the α–β transition of K_5ThF_9 and by 30—40° for the α–β transition of K_2ThF_6.

Where incongruent or near-incongruent melting systems were found, it was noted that arrests appeared at unexpected positions on the cooling curves, *e.g.*, at temperatures corresponding to eutectics or incongruent m. p.s of adjacent compounds (Figs. 2 and 3). This behaviour was attributed to incomplete establishment of equilibrium between the liquid and interacting solid during the cooling period.

After fusion, the composition of mixtures was checked by analysis at a number of points on the phase diagram. No significant departure from the calculated compositions was detected.

For the study of certain lower-temperature transitions a method of differential thermal analysis was used. The furnace and nickel sample block were as described by Berkelhamer (Tech. Paper 664, 1945, U.S. Bur. Mines). The sample (0·45 g.) was heated at a uniform rate of 8° per min., calcined alumina being used as a reference material. The output of the platinum–platinum-rhodium differential thermocouple was amplified and recorded on a strip chart potentiometer responsive to rapid changes in applied voltage. High amplification of the differential temperature was necessary to obtain a clear record of the thermal changes of the substance K_3ThF_7.

(b) *Analysis by optical examination of quenched melts.* This technique (Rankin and Wright, *Amer. J. Sci.*, 1915, **39**, 1; Faust, *Amer. Min.*, 1936, **21**, 735) is of particular value in the study of systems subject to a high degree of supercooling, and it has been employed in the study of the system $KF–ThF_4$ where the thorium fluoride content of the melts exceeded 70 moles %. In these melts the degree of supercooling of the liquidus, even with vigorous stirring, was so large (of the order of 100° with pure thorium fluoride) that location of liquidus points by thermal analysis alone became impossible.

The equipment consisted of a vertical alumina tube furnace, a thermocouple and potentiometer for temperature measurement, and a controller of special design for maintaining furnace temperatures within ±0·5°. A holder for the thermocouple and lead-in wires adequately sealed the upper end of the furnace tube. The lower end was provided with a stopper carrying a tube for admission of oxygen-free argon. The usual procedure consisted in wrapping a sample weighing several mg. in thin platinum foil and suspending the foil by thin (0·002 in.) platinum wire from heavier-gauge platinum leads through which current from a battery could be passed. The hot junction of the thermocouple was close to the suspended sample. After the charge had been kept for a suitable time at the required temperature the lower end of the furnace tube was opened, and the battery switch was closed to fuse the suspension and drop the charge into a bath of cold water. In the system $KF–ThF_4$ liquids did not quench to glasses but to crypto-crystalline material which was readily distinguishable from the larger and usually better-formed crystals that represented the solid phase in the system solid + liquid. Macrocrystalline phases present in the quenched specimens were distinguished by optical microscopy.

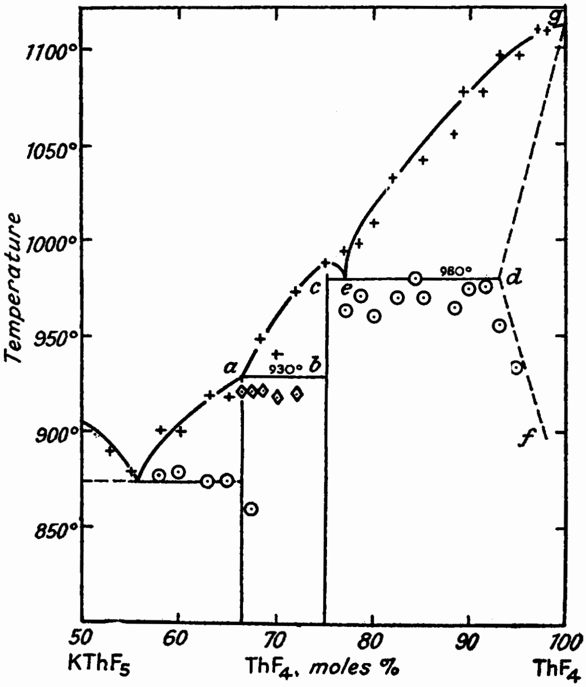


FIG. 3. *The system* $KThF_5–ThF_4$.
(Liquidus curves at ThF_4 concentrations exceeding 70 moles % obtained from quenching experiments. Position of eutectic lines *ab* and *cd* in accordance with quenching data shown 10—15° above points obtained from cooling curves.)

The results of the thermal and quenching studies are presented as a phase diagram of the system in Figs. 1, 2, and 3. Optical properties of various compounds are summarised in Table 1, which also compares densities determined in pure benzene with values calculated by Zachariasen. The density and optical properties of α-K_5ThF_9 and K_3ThF_7 could not be determined, as α-K_5ThF_9 reverted to the β-form when quenched, while K_3ThF_7 disproportionated into other compounds.

Precipitation of Potassium Thorium Fluorides from Aqueous Solution.—A systematic study of the precipitated phases was made. The sparingly soluble binary fluorides were obtained at 20°

TABLE 1. *Optical properties of anhydrous potassium thorium fluorides.*

							ρ_{25}	
Phase	Crystal system *	α or ϵ	γ or ω	D.R.	$2V$	Sign	This investigation	Zachariasen
ThF_4	Monoclinic	1·494	1·526	0·032	64°	+ve	6·29	6·14 †
KTh_3F_{13}...	Hexagonal	1·519	1·536	0·017	Uniaxial	−ve	6·23	—
KTh_2F_9 ...	Orthorhombic	1·490	1·532	0·042	16°	−ve	6·09	6·04
$KThF_5$ ...	Rhombohedral	1·470	1·475	0·005	Uniaxial	−ve	5·23	5·10
β-K_2ThF_6	Hexagonal	1·488	1·463	0·025	Uniaxial	+ve	4·82	4·91
α-K_2ThF_6	Cubic	1·45(5) ‡	—	—	—	—	—	4·33
β-K_5ThF_9	Orthorhombic	1·397	1·403	0·006	High	−ve	3·60	3·58
KF	Cubic	1·352	—	—	—	—	2·50	2·54 †

* Except for KF after Zachariasen (*loc. cit.*) and MDDC–1151, 1947. † Calc. from X-ray data.
‡ Determined on precipitated material dried at 300°.

by adding potassium fluoride to thorium nitrate, or by adding hydrofluoric acid to mixtures of thorium nitrate and potassium nitrate. Fluoride added was equivalent to the total potassium and thorium, and, except in the first four experiments in Table 3, sufficed to complete precipitation of M/30-quantities of thorium in a total volume of 250—300 ml. Unless stated otherwise, the precipitant was added dropwise in the above order in approximately 4 minutes. In general, voluminous gels were formed at first. After 15 hours these became dense and powdery.

The results of the precipitation studies are presented in Tables 2 and 3. The minute state of subdivision of the binary compounds (1—3 microns) precluded adequate determination of their optical properties. However, under high magnification (×980) aggregated products containing KTh_2F_9 or $KThF_5$ were seen to be anisotropic. Products containing as a major phase the compound α-K_2ThF_6 consisted of larger, spherical aggregates which were substantially isotropic. Freshly precipitated thorium fluoride gels dried in air consisted of amorphous, isotropic material, but specimens aged for 15 hours or more in solutions containing excess of hydrofluoric acid showed a fibrous or fascicular structure. The fibres, which were anisotropic and showed straight extinction along the fibre axis, served to identify aged samples of the hydrated fluoride. Because of the limited information obtainable from optical observation of the precipitates, an X-ray report on the various potassium thorium fluorides was obtained from Dr. A. McL. Mathieson. The powder data were obtained with nickel-filtered copper radiation. The cell dimensions of the various potassium thorium fluorides have been given by Zachariasen (*loc. cit.*) but intensity data were not reported. Identification was therefore based on the agreement of observed spacings with those calculated from the cell dimensions. Phases identified by this method are given in col. 3 of Tables 2 and 3.

TABLE 2. *Potassium thorium fluorides precipitated by hydrofluoric acid from mixtures of potassium and thorium nitrates. Products dried for* 15 *hr. at* 110°.

Molecular ratio:				Phases identified by X-ray examination:	
KNO_3 :	$Th(NO_3)_4$:	HF	Composition of product	major	minor
110	1	114	$K_{1\cdot15}ThF_{5\cdot18},0\cdot28H_2O$	α-K_2ThF_6	KTh_2F_9
50	1	54	$KTh_{0\cdot996}F_{5\cdot14},0\cdot27H_2O$	α-K_2ThF_6	KTh_2F_9
20	1	24	$KTh_{1\cdot25}F_{6\cdot10},0\cdot45H_2O$	α-KTh_2F_9	α-K_2ThF_6
10	1	14	$KTh_{1\cdot61}F_{7\cdot46},0\cdot70H_2O$	KTh_2F_9	—
5	1	9	$KTh_{1\cdot75}F_{8\cdot04},0\cdot89H_2O$	KTh_2F_9	—
2	1	6 (*a*)	$KTh_{2\cdot01}F_{8\cdot81},0\cdot88H_2O$	KTh_2F_9	—
—	—	— (*b*)	$KTh_{1\cdot92}F_{8\cdot69},1\cdot60H_2O$	KTh_2F_9	—
1	1	5	$KTh_{2\cdot00}F_{8\cdot90},0\cdot87H_2O$	KTh_2F_9	—
1	2	9 (*c*)	$KTh_{2\cdot75}F_{12\cdot0},2\cdot68H_2O$	KTh_2F_9	(ThF_4,nH_2O) *
—	—	— (*d*)	$KTh_{3\cdot39}F_{14\cdot1},2\cdot54H_2O$	KTh_2F_9	(ThF_4,nH_2O) *
1	5	21	Gel obtained only	—	—
1	10	41	$K_{0\cdot071}ThF_{4\cdot06},0\cdot90H_2O$	(ThF_4,nH_2O) *	KTh_2F_9

(*a*) $Th(NO_3)_4$ added to KNO_3 + HF. (*b*) Same order of precipitation as in (*a*); air-dried at 20°. (*c*) Air-dried. (*d*) Washed with 0·1N-HNO_3, then water, and air-dried.

* Phase not identified by X-ray examination; presence of ThF_4 deduced from analysis and/or microscopic examination.

Examination of anhydrous thorium fluoride showed products obtained by dehydration of the precipitated fluoride, or by fluorination of thorium oxide with ammonium fluoride, to be identical. Gelatinous thorium fluoride gave no powder pattern, but the fibrous hydrate, containing 2—3 moles of water, gave a pattern with a long spacing of 17 Å which could not be identified.

Dehydration of Hydrated Fluorides.—A small platinum boat containing the fluoride was placed in a platinum tube and heated in a current of dry air. Both the loss in weight of the fluoride and the hydrofluoric acid evolved on heating were determined, the acid vapours being conducted through polythene tubing into dilute sodium hydroxide· Fluorine was then determined by titration with thorium nitrate. Trial experiments using 7 mg. quantities of pure hydrofluoric acid gave fluorine recoveries of not less than 97%. The composition of the samples used was approximately as follows, only the fluorine and water contents being known exactly: (I) $KThF_5,nH_2O$ (25·0%F), (II) KTh_2F_9,nH_2O (24·5% F), and (III) ThF_4,nH_2O (20·5% F). Water in these samples was determined by igniting them with litharge and weighing the water evolved. Samples were first dried in air, (I) and (II) at 105° and (III) at 20°. Table 4 shows the results obtained.

TABLE 3. *Potassium thorium fluorides precipitated by potassium fluoride from thorium nitrate. Products dried for* 15 *hr. at* 110°.

Molecular ratio:		Phases identified by *X*-ray examination:	
KF : $Th(NO_3)_4$	Composition of product	major	minor
0·3	No precipitate	—	—.
1·0	No precipitate	—	—
1·5	Opalescence only	—	—
3·0 †	$K_{0·03}ThF_{3·99},2·22H_2O$	(ThF_4,nH_2O)*	—
4·0	$KTh_{2·38}F_{10·5},0·98H_2O$	KTh_2F_9	—
5·0	$KTh_{0·99}F_{4·87},0·43H_2O$	α-K_2ThF_6 ‡	(KTh_2F_9) *
10·0	$K_{1·27}ThF_{5·19},0·29H_2O$	α-K_2ThF_6	—
20·0 (*a*)	$K_{1·45}ThF_{5·53},0·53H_2O$	α-K_2ThF_6	$KTh_2F_9 + KThF_5$
— (*b*)	$K_{1·59}ThF_{5·58},0·59H_2O$	α-K_2ThF_6	$KThF_5$
40·0 (*c*)	$K_{1·59}ThF_{5·57},0·25H_2O$	α-K_2ThF_6	—

(*a, b, c*) $Th(NO_3)_4$ added to KF: (*a*) rapidly (0·5 min.), (*b*) slowly (2 hr.).
* See Table 2, footnote (*). † Precipitation incomplete.
‡ On a second occasion KTh_2F_9 was identified as major phase.

Analytical Methods.—All samples prepared by precipitation were decomposed by fuming in platinum dishes with concentrated sulphuric acid. The bulk of the excess of acid was finally volatilised. All samples prepared by fusion required heating with ammonium fluoride before fuming with sulphuric acid and ammonium sulphate.

TABLE 4. *Loss of water and hydrogen fluoride from hydrated fluorides on heating.*

Sample	Temp.	Time, hr.	Wt. loss, %	F loss, % of total F	Sample	Temp.	Time, hr.	Wt. loss, %	F loss, % of total F
* $KThF_5,nH_2O$	300°	1	2·37	nil	† KTh_2F_9,nH_2O	300°	2	2·72	0·12
	,,	2	2·52	0·008		400	2	3·02	0·46
	,,	4	2·59	0·024					
	400	1	2·64	0·096	‡ ThF_4,nH_2O ...	300	2	15·3	0·16
	,,	2	2·60	0·16		,,	4	15·5	0·30
	,,	4	2·64	0·17					

H_2O, determined by litharge method: * 2·47, † 3·09, ‡ 15·5%.

(i) Thorium in the clear aqueous extracts was precipitated by slow addition of 10% oxalic acid solution at 80°. The oxalate was then ignited to oxide and weighed. Results accurate to within 1—2 parts in 750 were obtained by this procedure.

(ii) Potassium in the thorium-free filtrate was determined as the sulphate after excess of oxalic acid had been destroyed by fuming with sulphuric acid. Residual ammonium sulphate was volatilised at 750° Negligible loss of potassium occurred through co-precipitation with thorium oxalate.

(iii) Water was at first determined by heating the various fluorides with ignited litharge and collecting the water evolved. All later determinations were made by measuring the loss in weight of the fluorides after 3 hours at 300°.

(iv) Residual nitrate in the precipitated fluorides was reduced with Devarda's alloy and determined as ammonia.

(v) Fluorine in the binary fluorides was determined by Willard and Winter's procedure, 50% sulphuric acid being used to volatilise fluorosilicic acid. Fused samples were given a preliminary fusion with sodium hydroxide. Reagent-grade sodium fluoride used as a titrimetric standard was analysed by conversion into sodium sulphate and by heating to constant weight at

750°. It was found to contain 99·2% of sodium fluoride and 0·70% of water. The reliability of the distillation and titration techniques for fluorine was checked with a U.S. Bureau of Standards analysed sample of fluorspar, which was distilled with perchloric acid, and a sample of Greenland cryolite, which was distilled with sulphuric acid. Results in agreement with the calculated fluorine contents of these samples were obtained.

Use of perchloric acid for distillation of fluorine from thorium fluoride caused recovery of only 60—80% of the fluorine recoverable by distillation, under similar conditions, with sulphuric acid. Preliminary fusion with sodium hydroxide did not increase the fluorine recovery. It is presumed that complexes between thorium and fluoride ions (see p. 4479) hinder volatilisation of fluorosilicic acid, absence of the effect with sulphuric acid probably resulting from precipitation of sparingly soluble hydrates of thorium sulphate during the distillation process.

Fluorine in pure thorium fluoride was checked by two independent methods of analysis since the stoicheiometric ratio of fluorine to thorium was never attained in products analysed by Willard and Winter's procedure. Usually this ratio was in the range 3·95—3·99. Fischer and Peisker's method (*Z. anal. Chem.*, 1933, **95**, 225) gave results in good agreement with those obtained by Willard and Winter's procedure. Allowance was made for the increased solubility of lead chlorofluoride in sodium nitrate, derived from the fusion mixture used to decompose the sample. Warf's method ("The Analytical Chemistry of the Manhattan Project," edited by C. J. Rodden, p. 729, McGraw-Hill, New York, 1950), involving pyrohydrolysis of thorium fluoride at 1000° in a current of steam in a platinum tube and simple titration of hydrofluoric acid in the condensate, gave ratios of fluorine to thorium virtually identical with the theoretical value. Care was needed, however, to prevent carry-over of solid products into the condensate. Allowance was made for nitric acid volatilised from thorium fluoride containing nitrate impurities. It was concluded that classical methods of fluorine analysis are subject to error when applied to pure thorium fluoride, giving results approximately 1·5% low even if all precautions have been taken. For this reason Warf's method was finally adopted for analysis of thorium fluoride. It has the advantage that the thorium content of the sample can be simply determined by weighing residual thorium oxide.

DISCUSSION

(i) *Thermal Analysis of the System* $KF-ThF_4$.—Six compounds have been shown to exist in the system $KF-ThF_4$ (Fig. 1), *viz.*, the congruently melting compounds K_3ThF_7, K_2ThF_6, $KThF_5$, KTh_2F_9, and KTh_3F_{13}, and the incongruently melting compound K_5ThF_9.

The sub-system $KF-K_5ThF_9$. Pure potassium fluoride synthesised from analytical-grade reagents melted at 856° ± 2°, in agreement with Bergman and Dergunov (*Doklady Acad. Nauk. S.S.R.*, 1941, **53**, 753). The reagent-grade product melted at 852°. The melting point is lowered rapidly by addition of thorium fluoride until the eutectic composition is reached at 694° (14 moles % of thorium fluoride). The compound K_5ThF_9 was found to be dimorphic, the high-temperature or α-form melting incongruently at 712° and changing sharply at 635° into a low-temperature form. The compound described by Zachariasen is therefore the β-phase. The experimentally determined density of β-K_5ThF_9 agrees satisfactorily with the value calculated from the cell constants (Table 1). β-K_5ThF_9 is hygroscopic and is decomposed by water.

The sub-system $K_5ThF_9-K_3ThF_7-K_2ThF_6$. Addition of thorium fluoride to K_5ThF_9 raises the liquidus of the system to a clearly defined maximum at 865° (25 moles % of thorium fluoride), thus confirming the peak found by Bergman and Dergunov (25 moles %, 870°) and establishing the existence, at higher temperatures, of the compound K_3ThF_7. Further addition of thorium lowers the liquidus of the system to a eutectic at 691° (31 moles % of thorium fluoride) between K_3ThF_7 and α-K_2ThF_6.

Weak arrests on the heating curves of mixtures containing approximately 25 moles % of thorium fluoride suggested a thermal change in the compound K_3ThF_7 at approximately 590°. Unequivocal evidence for this change was obtained from a differential thermal analysis of a previously fused mixture of the stoicheiometric composition. A sharp endothermic peak rising from 570° to a maximum at 600° was obtained on the heating curve, and a broader, exothermic peak rising from 575° to a maximum at 545° appeared on the cooling curve. The areas of these peaks were approximately equal. Weaker thermal effects were obtained at approximately these temperatures with mixtures within the ranges of composition 16·6—25 and 25—33·3 moles % of thorium fluoride, respectively, but no thermal effects below 600° were detected at the compositions K_5ThF_9 or K_2ThF_6. When the solid reaction product of overall composition K_3ThF_7 was kept at 700° for 20 hours and then rapidly quenched, *X*-ray powder photographs showed the presence of β-K_5ThF_9. Lines corresponding to this latter phase were broad in the high sin θ region. Also shown on the photographs were lines, very sharp up to the limit of sin θ, which presumably correspond to the phase K_3ThF_7. It was impossible to differentiate lines corresponding to K_3ThF_7 from those of β-K_5ThF_9 in the low-angle region, and hence impossible to determine the crystal structure of this phase. If the quenched sample was rephotographed several days later the pattern of β-K_5ThF_9 was found to have faded and the dominating pattern was that of β-K_2ThF_6 with, however, an expanded unit cell, $a = 6{\cdot}645$ and $c = 3{\cdot}845$ Å, compared with the normal cell dimensions 6·571 and 3·817 Å, respectively. Evidently the phase K_3ThF_7 disproportionates at approximately 570° : $3K_3ThF_7 \longrightarrow \beta\text{-}K_5ThF_9 + 2\beta\text{-}K_2ThF_6$. Initially, the mixture of disproportionation products contains residual K_3ThF_7, large crystals of which give the very sharp diffraction lines. It is possible that transition from K_3ThF_7 to β-K_5ThF_9 is relatively easy compared with that from K_3ThF_7 to β-K_2ThF_6, since the bulk of the initially formed mixture appears to consist of smaller crystals of β-K_5ThF_9 and particles of the expanded form of β-K_2ThF_6 which are less than 100 Å in diameter. After several days, when disproportionation is complete, the expanded form of β-K_2ThF_6 increases in particle size until this substance dominates the diffraction pattern.

The density of the reaction products ($\rho_{25} = 4{\cdot}03$) agrees satisfactorily with that calculated for complete disproportionation of K_3ThF_7. The optical properties of these products are, however, anomalous. Thus the mixture containing 25% of thorium fluoride is apparently homogeneous under the microscope. The birefringence of the quenched mixture is very low, the product resembling a compound with refractive indices $\alpha = 1{\cdot}410$ and $\gamma = 1{\cdot}412$. It is presumed that the minute crystal size of both β-K_5ThF_9 and β-K_2ThF_6 causes the mixture to simulate an isotropic compound. If, however, the products are heated for at least 30 hours at 500° in an inert atmosphere and then cooled, crystal growth occurs and the apparently homogeneous mixture breaks up into its visibly anisotropic components. The area of the differential temperature peak at the disproportionation temperature suggests that the heat evolved in the above reaction is approximately 6 kcal. per mole of K_3ThF_7.

The compound K_2ThF_6 is the second of its type in the system KF–ThF_4 to exist in polymorphic forms. The α-phase melts at 747° and on cooling reverts sharply at 645° to the β-form. The density of cold melts containing 33 moles % of thorium fluoride was in approximate agreement with the value calculated by Zachariasen for β-K_2ThF_6 Attempts to obtain the α-phase by quenching at precisely the stoicheiometric composition were unsuccessful, but samples quenched from near this composition gave sufficient of the α-phase for optical examination. A disordered form of β-K_2ThF_6 has been reported by Zachariasen but no thermal effect ascribable to an order–disorder transition in β-K_2ThF_6 was detectable by differential thermal analysis.

The sub-system K_2ThF_6–KTh_2F_9. A well-defined maximum on the liquidus of this system at 905° denotes the compound $KThF_5$. A simple eutectic between $KThF_5$ and KTh_2F_9 is formed at 875° (56 moles % of thorium fluoride). The compound KTh_2F_9 is just able to melt congruently at 930°. Neither $KThF_5$ nor KTh_2F_9 shows evidence of polymorphism.

The sub-system KTh_2F_9–ThF_4. Bergman and Dergunov, and also Zachariasen, both report a compound between thorium fluoride and the composition 66 moles % of thorium fluoride, the former claiming its composition to be KTh_3F_{13} and the latter to be KTh_6F_{25}. The composition KTh_6F_{25} does not explain the results of the quenching experiments. Because of the determined liquidus a compound KTh_6F_{25} should have an incongruent melting point and be stable below the line *cd* (Fig. 3), the approximate position of which has been verified by quenching experiments and by cooling curves. However, charges of the composition KTh_6F_{25} held for periods of 1—2 hours at temperatures below the line *cd* showed no trace of fusion and consisted of a mixture of the monoclinic solid solution of thorium fluoride and a hexagonal phase. The hexagonal phase therefore cannot have the composition KTh_6F_{25}. Quenched charges of compositions containing 78·5 moles % or more of ThF_4 contained this compound as a primary phase. In quenches containing 77 moles % or less of ThF_4, the primary phase was a uniaxial compound which frequently exhibited well-developed hexagonal cross-sections under the microscope. The presence of these crystals above the line *cd* indicated a congruent m. p. for this compound. The position of the eutectic *e* (980°, 78 moles % of ThF_4) was determined from the position of the line *cd* and the change in primary phase between 77 and 78·5 moles % of ThF_4. The quenching data gave figures 10—15° higher than did the cooling curves for the eutectic lines *ab* and *cd*. The data therefore indicate that the hexagonal crystals were of the composition KTh_3F_{13} reported by Bergman and Dergunov. This compound, however, was found to melt at 990°, some 20° above the value found by them. Solid solution between KTh_3F_{13} and thorium fluoride is shown by the increasingly small interval between solidus and liquidus in the range of compositions 93—100 moles % of thorium fluoride, and by the presence of a uniphase solid at all points in the area *fdg*. Only in the area *bcdf* does the hexagonal phase appear with the solid solution phase. The extent of solid solution of the compound KTh_3F_{13} in thorium fluoride was not accurately determined but was of the order of 30%. No evidence for solid solution in this system has been presented by other investigators.

Pure thorium fluoride was found to melt at 1111° ± 2° : Bergman and Dergunov give 1114°. Fusion of thorium fluoride in the quenching furnace readily caused formation of the oxyfluoride, $ThOF_2$, or the oxide unless all traces of moisture and oxygen were excluded. Almost complete conversion into these highly refractive phases occurred if the fluoride was heated in air in an open crucible. Thorium oxide was the final product. Compositions containing potassium fluoride appeared to absorb oxygen less readily, particularly below 90 moles % of thorium fluoride. The structures of both thorium fluoride and thorium oxyfluoride have been determined by Zachariasen (*Acta Cryst.*, 1949, **2**, 388).

(ii) *Isolation of Potassium Thorium Fluorides from Aqueous Solutions.*—Precipitation studies in the systems $KF–Th(NO_3)_4–H_2O$ and $KNO_3–Th(NO_3)_4–HF–H_2O$ reveal a complicated behaviour attributable to complex formation between thorium and fluoride ions. Dodgen and Rollefson (*J. Amer. Chem. Soc.*, 1949, **71**, 2600) have shown that the ionic species in acid solutions containing thorium and fluoride ions are ThF^{3+}, $ThF_2{}^{2+}$, and $ThF_3{}^{1+}$, the ion $ThF_2{}^{2+}$ being the dominant ion at the point of precipitation of hydrated thorium fluoride. Day and Stoughton, however (A. E.C.D. 2756, 1949), found more probable formulæ for the complex ions to be $ThF(NO)_3{}^{2+}$ and $ThF_2(NO_3)^{1+}$. Whichever formulation of the complex ions is most appropriate, it is clear that association of fluoride ion with thorium so alters the fluoride-ion concentration that mixing of given molar proportions of potassium, thorium, and fluoride ions results in the precipitation of a binary fluoride differing markedly from the expected composition (cf. Tables 2 and 3).

Thorium fluoride, in addition to the compounds α-K_2ThF_6, $KThF_5$, and KTh_2F_9 isolated by earlier workers, has been isolated from solution. All other phases were decomposed by water to more stable substances. In the majority of cases mixtures of two or more phases were obtained, phases approximating in composition to $KThF_5$, for example, often consisting of KTh_2F_9 and α-K_2ThF_6 in approximately equal proportion. In general, solutions of low potassium fluoride, or low potassium fluoride plus nitric acid concentration, gave soluble fluoride complexes, or else yielded thorium fluoride as the insoluble phase. As the potassium fluoride concentration was increased, thorium fluoride was succeeded as solid phase first by KTh_2F_9 and then by α-K_2ThF_6. As found by Zachariasen, α-K_2ThF_6 was the major phase formed in all solutions rich in potassium fluoride, whether nitric acid was present or not.

The compound $KThF_5$ could not be isolated by observing conditions stated by Zachariasen, nor was it obtained at the expected composition between K_2ThF_6 and KTh_2F_9. It was obtained, however, in admixture with these compounds, in products precipitated in the absence of nitric acid by a large excess of potassium fluoride (Table 3). This suggests that it can be readily transformed into KTh_2F_9 by the action of nitric acid.

That KTh_2F_9 can also be changed in composition by the action of nitric acid is shown by the results in Table 2 for precipitations with potassium, thorium, and fluorine in molar ratios 1 : 2 : 9. The effect of nitric on the composition of the precipitate can be explained by the nature of the equilibrium between thorium and fluoride ions, this equilibrium, and hence the solubility product of the precipitates, depending on the hydrogen ion concentration.

Contrary to recent statements in the literature, all the precipitated phases were found to be hydrated, usually retaining 1 or 2 moles of water per mole of thorium fluoride when dried in air to constant weight, and less than 1·0 mole of water after drying for 15 hr. at 110°. Gelatinous thorium fluoride, however, retained 2·5—3·5 moles of water when air-dried and 1—2 moles when oven-dried under similar conditions. As *X*-ray powder photographs of precipitated thorium fluoride could not be obtained unless the product was sufficiently aged, it may be noted that detection of this phase in mixtures is not always possible.

Dehydration of thorium fluoride and of the binary fluorides without appreciable loss of fluorine may be completed at atmospheric pressure by heating them for approximately 3 hours at 300° (Table 4). At higher temperatures fluorine is lost, presumably as hydrofluoric acid, and increasing quantities of oxyfluoride and oxide are formed. Loss of fluorine appears to occur more readily from thorium fluoride than from the potassium thorium fluorides.

(iii) *Structure of the Potassium Thorium Fluorides.*—With the exception of the compounds α- and β-K_2ThF_6 (Zachariasen, *loc. cit.*; *Acta Cryst.*, 1949, **2**, 388), little detailed knowledge exists of the structure of the potassium thorium fluorides. There are, however, many points of similarity between the systems KF–ThF_4 and KF–UF_4 (Zachariasen, *loc. cit.*). Much simpler systems characterised by a few structures stable over a wide range of composition are formed if the central ion is much smaller than the potassium or thorium ions, *e.g.*, in the system KF–MgF_2 (Remy and Seemann, *Rec. Trav. chim.*, 1940, **59**, 516), or if the central ion is comparable in size to these ions, *e.g.*, in the system KF–LaF_3 (Zachariasen, *loc. cit.*). The exceptional complexity of the systems KF–ThF_4 and KF–UF_4 appears to be largely due to the values of the radius ratios K : Th and K : U, which fall between the ratios K : Mg and K : La.

There is no evidence that water in the precipitated binary fluorides plays an essential part in the structure of the compounds as the structures of the fused and of the precipitated fluorides are virtually identical. Water, however, may exert a stabilising influence on the structure of α-K_2ThF_6 since this phase if anhydrous should not be stable below 645°. Indeed, if water is completely removed from α-K_2ThF_6 by heating it to 300°, differential thermal analysis shows that the fluoride reverts *exothermically* to the β-form at approximately 400°. This product then undergoes the usual endothermic β- to α-transition at the equilibrium transition temperature of 645°. Many other binary potassium fluorides, *e.g.*, those of titanium, zirconium, and tin, resemble the potassium thorium fluorides in containing 1—2 moles of water which do not appear to form an essential portion of the crystal structure. Water in the thorium compounds, and possibly in analogous compounds, is presumed to occupy vacant sites in the crystal structures and may therefore be described as "lattice water."

For *X*-ray reports on various precipitated and other fluorides the authors gratefully acknowledge their indebtedness to Dr. A. McL. Mathieson of the Chemical Physics Section of this Division.

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DIVISION OF INDUSTRIAL CHEMISTRY, MELBOURNE, AUSTRALIA. [*Received, June 3rd,* 1952.]