

Choppin and Padgitt³ the boiling point-composition curve has been determined.

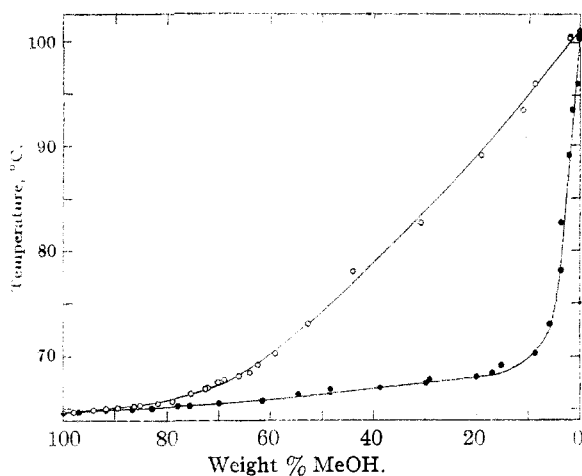


Fig. 1.—Vapor phase, O; liquid phase, ●.

The methyl alcohol and dioxane were purified as previously described³; the apparatus used was that of Othmer.⁴ Equilibrium between the vapor and liquid phases was established after

TABLE I
BOILING POINT-COMPOSITION DATA FOR THE METHYL ALCOHOL-DIOXANE SYSTEM AT ONE ATMOSPHERE

B. p., °C.	Wt., % liquid	MeOH vapor
64.60	100	100
64.72	96.5	98.1
64.90	91.9	94.2
64.96	86.7	91.9
65.10	82.9	89.4
65.27	78.0	86.3
65.34	75.7	85.2
65.55	69.7	81.7
65.78	61.7	77.9
66.50	54.6	75.7
66.94	48.4	72.6
67.10	38.8	72.2
67.60	29.8	70.2
67.89	29.0	67.9
68.20	20.0	66.1
68.50	17.0	63.9
69.30	15.4	62.5
70.40	9.7	59.0
73.20	6.0	52.7
78.20	3.9	44.1
82.80	3.7	30.8
89.20	2.4	19.1
93.50	1.6	11.1
96.04	0.7	8.7
100.38	.3	1.9
100.54	.3	1.8
101.05	.0	0.0

(3) Amis, Choppin and Padgitt, *THIS JOURNAL*, **64**, 1207 (1942).

(4) Othmer, *Ind. Eng. Chem.*, **20**, 743 (1928).

about three hours for each determination. Temperatures were measured with calibrated thermometers graduated in 0.05° with a precision of $\pm 0.05^\circ$. The liquid and vapor phases were analyzed by means of refractive index using the values reported by Amis, Choppin and Padgitt.³ The results are tabulated in the table and represented graphically in the figure.

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Addition Compounds of Tetrahydrothiopyran

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Two addition compounds of tetrahydrothiopyran (pentamethylene sulfide) and inorganic metal salts have been reported: $\text{HgCl}_2 \cdot (\text{CH}_2)_5\text{S}$ by Grischkewitsch-Trochimowski¹ and $x\text{HgI}_2 \cdot (\text{CH}_2)_5\text{S}$ by Bost and Conn.² This sulfide forms addition compounds with other metal halides, offering comparison with dithiane,³ dioxane,⁴ and morpholine.⁵ Tetrahydrothiopyran exhibited less tendency to form addition compounds than did dithiane or dioxane, but greater tendency than morpholine.

The compounds are crystalline, somewhat sensitive to water, and are white, except for the yellow gold(III) chloride, tin(IV) bromide, and platinum(II) iodide, the red-brown gold(III) bromide, and the orange-red palladium(II) chloride compounds. There was some indication of reaction with silver iodide, silver bromide, and tin(IV) iodide, but no compounds could be isolated. The following compounds gave no results: copper(II) fluoride, cadmium halides, zinc chloride, iron(III) chloride, arsenic(III) iodide, antimony(III) iodide and chloride, germanium(IV) chloride, and silicon(IV) chloride.

The thiopyran was prepared by a modification of the methods of von Braun⁶ and Clarke,⁷ using 100 g. of benzoylpiperidine and 110 g. of phosphorus pentachloride. The benzonitrile was hydrolyzed by warming under reflux, the dichloropentane steam distilled, and converted to tetra-

(1) Grischkewitsch-Trochimowski, *Chem. Zentr.*, **87**, I, 1503 (1923).

(2) Bost and Conn, *Ind. Eng. Chem.*, **23**, 93 (1931).

(3) Bouknight and Smith, *THIS JOURNAL*, **61**, 28 (1939).

(4) Rheinboldt, Luyken and Schmittmann, *J. prakt. Chem.*, **149**, 30 (1937).

(5) Haendler and Smith, *THIS JOURNAL*, **63**, 1164 (1941).

(6) von Braun, *Ber.*, **37**, 2915 (1904).

(7) Clarke, *J. Chem. Soc.*, **101**, 1785 (1912).

TABLE I
ADDITION COMPOUNDS OF TETRAHYDROTHIOPYRAN

Inorg. salt	Solvent	Solubility	M. p., °C.	Formula	Metal analyses, %	
					Calcd.	Found
HgBr ₂	Alcohol	Sl. sol. hot aq. alc.	101-105	HgBr ₂ ·(CH ₂) ₆ S	43.36	43.26
CuCl ₂	Alcohol	Ins. aq., org. solv.	154.5-157	CuCl·(CH ₂) ₆ S	31.59	31.55
Cu ₂ Cl ₂	Alc. HCl	Same	154.5-160	CuCl·(CH ₂) ₆ S	31.59	31.50
CuBr ₂	Alcohol	Same	123-124	CuBr·(CH ₂) ₆ S	25.88	25.85
Cu ₂ Br ₂	Alc. KBr	Same	121.5-122.5	CuBr·(CH ₂) ₆ S	25.88	25.79
Cu ₂ I ₂	Alc. KI	Same	164-165 d.	CuI·(CH ₂) ₆ S	21.73	21.85
HAuCl ₄	Ether	Sl. sol. alc., ins. eth.	120-122 d.	AuCl ₃ ·(CH ₂) ₆ S	48.60	48.39
HAuCl ₄	Alcohol	Ins. alc. eth.	179-182 d.	AuCl·(CH ₂) ₆ S	58.89	58.66
HAuBr ₄	Ether	Sl. sol. alc. eth.	140-145 d.	AuBr ₃ ·(CH ₂) ₆ S	36.58	36.70
^a	Alcohol	Sl. sol. hot alc.	173-179 d.	AuBr·(CH ₂) ₆ S	51.99	51.83
SnCl ₄	^b	Sol. chl., dec. aq.	149-151.5	SnCl ₄ ·2(CH ₂) ₆ S	25.53	25.57
SnBr ₄	Chlorof.	Sol. chl., dec. aq.	149.5-151	SnBr ₄ ·2(CH ₂) ₆ S	18.36	18.45
H ₂ PtCl ₆ -KI ^c	Alcohol	Ins. alc.	194.5-196 d.	PtI ₂ ·2(CH ₂) ₆ S	29.88	29.98
PdCl ₂	Acetone-H ₂ O	Sl. sol. acet., ins. aq.	146.5-148.5 d.	PdCl ₂ ·2(CH ₂) ₆ S	27.93	28.07

^a AuBr₃·(CH₂)₆S boiled with alcohol and excess thiopyran. ^b Thiopyran and tin(IV) chloride mixed directly. ^c Excess potassium iodide solution added to chloroplatinic acid in alcohol, precipitate dissolved by heating, and thiopyran added till no further precipitation.

hydrothiopyran by refluxing with excess sodium sulfide in ethanol.

The addition compounds were formed by dissolving the metal salt in ethanol or ether, adding salt or acid if necessary, and adding slight excess of sulfide, sometimes dissolved in the solvent. The data on the complexes are given in Table I.

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Structures of Complex Fluorides. Rubidium Hexafluogermanate

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In an earlier paper¹ we have reported the X-ray determination of structure for the isomorphous crystalline compounds potassium hexafluogermanate and ammonium hexafluogermanate, R₂GeF₆. Upon the basis of X-ray data obtained from a single specimen of what we supposed was rubidium fluogermanate, we stated at that time that this substance crystallizes in a more complex structural type than do the corresponding potassium and ammonium salts. This particular specimen occurred as a hexagonal prism, almost needle-like in shape, whereas we have since obtained only hexagonal tablets and plates by recrystallizing rubidium fluogermanate from aqueous solution at room temperature. X-Ray study of a number of these tabular crystals shows that they crystallize in the same structural type as do

(1) J. L. Hoard and W. B. Vincent, *THIS JOURNAL*, **61**, 2849 (1939).

potassium and ammonium fluogermanates. The single needle-like specimen may or may not have been rubidium fluogermanate: the values of the lattice constants indicate that it may have been a different crystalline modification of closely related and only slightly more complicated structure than that to be discussed here. In any case we must correct our earlier statement at least to the extent of asserting that the usual and presumably the stable form at room temperature of rubidium fluogermanate is fully isomorphous with the corresponding ammonium and potassium salts.

The X-ray data for Rb₂GeF₆ lead to a hexagonal unit cell with $a = 5.82$, $c = 4.79$ Å., space-group $D_{3d}^3 - C\bar{3}m$, containing one stoichiometric molecule. The atomic coordinates² are Ge in (a): 000; 2Rb in 2(d): $1/3$ $2/3$ u ; $2/3$ $1/3$ \bar{u} with $u = 0.695$; 6 F in 6(i): xxx , etc., with $x = 0.144$, $z = 0.213$.

The methods used in establishing this structure closely paralleled those previously described.¹ A comparison of calculated with observed reflection amplitudes for over one hundred forms in rubidium fluogermanate led to generally excellent agreement. Having presented¹ the corresponding data in detail for potassium fluogermanate, and ammonium hexafluogermanate, it seems unnecessary to reproduce the rather extensive tables³ for rubidium hexafluogermanate in this note. In addition we find that a Fourier projec-

(2) "Internationale Tabellen zur Bestimmung von Kristallstrukturen," Gebrüder-Borntraeger, Berlin, 1935, Vol. I, p. 258.

(3) The amplitude data for rubidium hexafluogermanate are available in the Thesis of W. B. Vincent, "The Structures of Some Fluosilicates and Fluogermanates," Cornell University Library, 1940.