biaxial positive with the interaxial angle, $2V$, approximately 60°. This angle was measured on the four-axis universal rotating stage. Chromatic dispersion of the crystals is weak with $2V$ for the red wave lengths greater than $2V$ for violet. In addition, the horizontal-type dispersion of the principal optic plane was recognizable, indicating that the obtuse bisectrix coincides with the b crystallographic axis. This agrees with the indicatrix orientation determined on the universal stage as follows:

$X = b$ crystallographic axis and the angle between Y and c crystallographic axis of $-2°$.

Two distinct habits of crystals are present in the sublimed material. One type is acicular and elongated on the c crystallographic axis. The other type is tabular parallel to the (010) pinicoid. The acicular crystals were studied first and optical properties were determined on them. Optical properties were checked later on the tabular crystals and were identical. The geometrical crystallography was worked out first on the acicular crystals, and then the tabular crystals were made to fit this geometry when the relationship between the two was recognized. No x-ray determinations were made.

The acicular crystals are dominated by the $a(100)$ and $b(010)$ pinicoids with a minor development of a third order prism, probably (110). The needles are terminated by two prisms, the larger of which was assigned as the first order prism $(0kl)$. The smaller then became a negative fourth order prism $(\bar{h}kl)$. In no crystal observed were both ends terminated so that the symmetry is either $2/m$ or m. The angle β between the a and c axes, as defined by the assigned first order prism, is approximately 115°. A very small negative second order $(\bar{h}0l)$pinicoid is present on some crystals. Many of the acicular crystals contain elongated gas cavities along the c crystallographic axis. Figure 3 is a sketch of these crystals and does not attempt to show interfacial angles closer than a few degrees. Stellate clusters of these crystals are common.

The tabular crystals are up to a millimeter in maximum dimensions but are very thin. They are dominated by the b pinicoid (010) with the edges truncated by a thin third order prism $(hk0)$ and a thin negative fourth order prism $(\bar{h}kl)$. Rounded elongated gas cavities are common in these plates with their long dimensions parallel to the negative fourth order prism zone. In some crystals, a transition from the tabular habit to the acicular habit can be seen by extension of growth along the c axis and the development of terminations identical to those of single acicular crystals. The $\bar{h}kl$ and $\overline{hk}l$ faces of the plate are then replaced with a saw-toothed edge as shown in Figure 4. In this growth process, the central gas cavity of the tabular crystals branches up the c crystallographic axis of each crystal.

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Properties of Constant-Boiling Hydrochloric Acid–Zirconyl Chloride Solutions

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No data were available on the effect of dissolved zirconyl chloride on the constant-boiling hydrochloric acid–water azeotrope. Therefore, measurements were made (at atmospheric pressure) of boiling points, incipient crystallization temperatures, densities, and chloride concentrations in boiling HCl–H_2O–0.2M to 3.5M $ZrOCl_2$. A decreasing HCl content with increasing $ZrOCl_2$ content maintained a nearly constant boiling point at about 111° C. Incipient crystallization temperatures increased from 41° to 95° C. with increasing $ZrOCl_2$ content.

BECAUSE data were needed on the effect of dissolved zirconyl chloride on the constant-boiling hydrochloric acid–water azeotrope, boiling points, incipient crystallization temperatures, densities, and chloride concentrations were measured at atmospheric pressure.

MATERIALS

Zirconyl chloride octahydrate was purchased from A. D. Mackay Co. The major impurities revealed by spectroscopic analyses were Si less than 50 p.p.m., Ca 10 p.p.m., and smaller amounts of Mg, Fe, and Cu. Reagent grade hydrochloric acid and distilled water were used to prepare solutions.

EXPERIMENTAL PROCEDURE

Zirconyl chloride–hydrochloric acid solutions were prepared by mixing $ZrOCl_2 \cdot 8H_2O$ with 9N HCl. Hydrochloric acid was distilled off at atmospheric pressure, using a single-plate distillation flask with a downdraft condenser. Distillation was continued until the volume in the distillation flask had decreased to the desired level. The boiling point was then monitored during a period in which the heating rate was decreased and the system approached total reflux. In no case was a change in boiling point detected during the last 10 minutes of this period. The 27 boiling points reported are those obtained as the system approached total reflux. Therefore, these boiling points may be considered to be the boiling points of constant-boiling HCl solutions containing specific concentrations of a third component, $ZrOCl_2$. It was necessary to determine boiling points in this way (by approaching total reflux during each determination) because the nonequilibrium conditions

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existing during distillation affect the boiling point, and because the increasing $ZrOCl_2$ concentrations in the residue during distillation were expected to affect the boiling point.

Heat was supplied through a rapidly stirred oil bath. The temperature was measured continuously with a copper-constantan thermocouple inserted into a glass tube that extended into the distillation flask. The thermocouple was connected, through junctions maintained at 0° C., to a Leeds & Northrup millivolt potentiometer. The thermocouple was calibrated at the freezing and boiling points of water. Boiling points were corrected from atmospheric pressure of about 745 to 760 mm. of Hg, using Craft's rule.

After each boiling point determination, the oil bath was cooled slowly (to avoid supercooling), and the temperature at which crystals began forming in the solution was determined both by observation and from inflections in the cooling curve. The distillation flask included a lower spherical chamber, which held most of the solution; an upper spherical chamber, which prevented the solution from bumping over during distillation; and a volume-calibrated cylindrical section connecting the upper and lower chambers. The volume of the solution was monitored during cooling by observing the liquid level in the calibrated portion of the flask.

The distilled hydrochloric acid was collected in dilute NaOH, and the alkaline product solution was analyzed for chloride. Water in the distillate was determined by subtracting the weight of HCl which distilled (calculated from the chloride analysis) from the weight loss of the solution (determined by weighing the distillation flask and contents on an analytical balance before and after distillation).

The distillation and cooling procedures were repeated several times until the volume of solution remaining approached the minimum that could be measured in the calibrated section of the distillation flask, about 60% of the initial volume.

The concentrations of hydrogen chloride, water, and zirconium in solution after each distillation were calculated by subtracting the amount that distilled (no zirconium distilled) from that present before distillation, and dividing by the volume at the temperature of incipient crystallization. Density was calculated by dividing the weight of the solution by its volume at the temperature of incipient crystallization. A series of eight runs, varying between about 0.2 and 2.3*M* in initial $ZrOCl_2$ concentrations, was made.

Chloride was determined by potentiometric titration with silver nitrate. Zirconium was determined gravimetrically after evaporation to dryness and ignition to form ZrO_2.

RESULTS

As the $ZrOCl_2$ concentration in the HCl-H_2O-$ZrOCl_2$ solutions (calculated at the temperature at which crystallization first occurred during slow cooling) increased from 0.2 to 3.5*M*, the temperature at which crystallization started increased irregularly from 41° to 95° C., the molar ratio of HCl to $ZrOCl_2$ decreased from 29 to 0.5, the molar ratio of H_2O to ZrO_2Cl_2 decreased from 214 to 13, the molar ratio of H_2O to HCl increased from 7 to 26, and the density increased from 1.13 to 1.54 (Table I and Figure 1). Results are presented in terms of the $ZrOCl_2$, HCl, and H_2O concentrations for convenience only. The actual structures of the solvated species or of the crystallized products were not investigated. The densities at the incipient crystallization temperatures fluctuated widely, particularly at $ZrOCl_2$ concentrations below 1.8*M*, where the incipient crystallization temperatures also fluctuated widely. The boiling point was 110.8° ± 1.3° C. at all $ZrOCl_2$ concentrations.

Table I. Properties of Boiled Zirconyl Chloride–Hydrochloric Acid Solutions, Measured at Time Crystallization Started upon Cooling

				Molar Ratios		
Run	$ZrOCl_2$, *M*	T, ° C.	Density	H_2O/$ZrOCl_2$	HCl/$ZrOCl_2$	H_2O/HCl
1-1	1.18	73.2	1.30	41.6	4.64	8.97
1-2	1.29	74.9	1.27	37.3	3.85	9.70
1-4	1.29	76.8	1.27	36.9	3.79	9.74
1-5	1.49	78.3	1.36	30.7	3.30	9.32
1-6	1.57	78.6	1.32	30.7	2.90	10.6
3-2	0.22	41.2	1.14	214.	29.4	7.29
3-3	0.23	41.1	1.13	212.	28.5	7.44
4-1	0.50	63.9	1.16	92.3	13.7	6.74
4-2	0.55	68.1	1.17	85.4	10.8	7.89
5-1	1.57	78.8	1.28	29.5	2.86	10.3
5-2	1.74	79.8	1.30	26.8	2.39	11.2
5-3	1.96	81.9	1.35	24.2	2.00	12.1
5-4	2.14	77.7	1.38	24.8	1.72	14.5
6-1	2.59	85.6	1.43	18.4	1.18	15.6
6-2	3.02	92.8	1.49	15.8	0.84	18.8
6-3	3.21	94.1	1.49	14.6	0.67	21.7
7-1	0.75	71.0	1.17	60.5	8.00	7.56
7-2	0.83	75.2	1.20	56.6	6.77	8.36
7-3	0.87	72.6	1.15	51.7	5.76	8.98
7-4	1.00	67.3	1.21	47.4	5.07	9.34
8-1	1.85	80.0	1.34	25.7	2.23	11.5
8-2	1.97	83.2	1.35	24.2	1.96	12.3
8-3	2.19	80.4	1.38	21.9	1.61	13.6
8-4	2.34	81.0	1.40	20.5	1.38	14.8
9-1	2.82	92.6	1.48	17.2	1.04	16.5
9-2	3.06	93.2	1.49	15.7	0.78	20.1
9-3	3.51	94.8	1.54	13.4	0.52	26.1

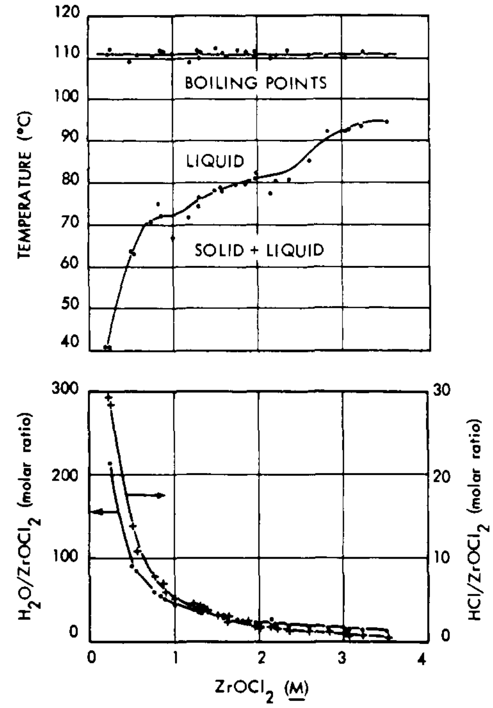

Figure 1. Properties of boiled zirconyl chloride–hydrochloric acid solutions

The percentage of water in the boiling solutions remained nearly constant, at 88.1 ± 1.8 mole %, as the zirconyl concentration increased from 0 to 6.7 mole % (Figure 2). The mole percentage of hydrogen chloride increased from 12.0 to 12.8, then decreased to 3.5. The point given for pure hydrochloric acid is that corresponding to 745 mm. of Hg pressure. The small variation in atmospheric pressure between runs (±6.0 mm. of Hg from the mean pressure of 745.8 mm. of Hg) should not have significantly affected the compositions of the boiling solutions.

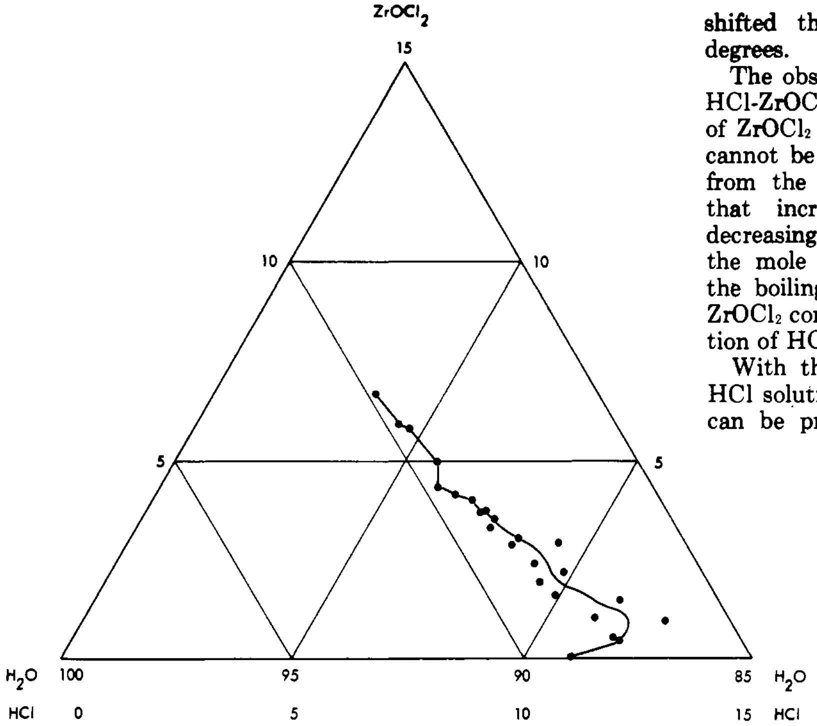

Figure 2. HCl-H_2O-$ZrOCl_2$ system at boiling points
In mole percentage

The reproducibility between runs, particularly in the temperature of incipient crystallization—see runs 5 and 8, for example—confirms that the measurements were indeed made on a reproducible azeotropic system, analogous to the two-component H_2O-HCl system, but containing a specific amount of a third component, $ZrOCl_2$. In experiments previous to those reported above, it was discovered that small deviations from the azeotropic HCl-H_2O ratio shifted the incipient-crystallization temperature several degrees.

The observation that the boiling point of the azeotropic HCl-$ZrOCl_2$ solutions was nearly constant over the range of $ZrOCl_2$ concentrations investigated was unexpected and cannot be fully explained at present. However, it is clear from the results, particularly as presented in Figure 2, that increasing $ZrOCl_2$ concentrations correspond to decreasing HCl concentrations and have little effect on the mole per cent of H_2O. Thus, the ionic strength of the boiling solutions must remain nearly constant as the $ZrOCl_2$ concentration increases. This is due to the volatilization of HCl.

With the aid of Figure 1, the properties of a $ZrOCl_2$-HCl solution that has been boiled at atmospheric pressure can be predicted at $ZrOCl_2$ concentrations up to 3.5*M*.

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Acid Ionization Constants of Phenol and Some Hydroxymethylphenols between 20° and 60° C.

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The temperature dependence of the acid ionization constants of phenol and four hydroxymethylphenols has been determined between 20° and 60° C. The pK_a at an ionic strength of 0.1 at 60° C. and the quantity $d(pK_a)/d(1/T)$ are: phenol 9.49, 1046; 2-hydroxymethylphenol 9.42, 1182; 4-hydroxymethylphenol 9.39, 981; 2,4-dihydroxymethylphenol 9.31, 1072; and 2,4,6-trihydroxymethylphenol 9.10, 991.

THE industrial preparation of phenolic resins of the "resole" type is based on the hydroxymethylation of phenol by formaldehyde; relatively small amounts of base, of the order of 5 mole % on phenol, are used to catalyze the reaction, usually at temperatures in the vicinity of 60° C. The intermediate products are the hydroxymethylphenols, having the general formula $HOC_6H_{5-n}(CH_2OH)_n$ ($n = 1$, 2, or 3), which also react with formaldehyde when $n = 1$ or 2. The rates of these reactions are proportional to the anion concentration of each phenolic species, and an exact knowledge of the acid ionization constants is necessary to establish the distribution of the anion form among phenol and the five hydroxymethylphenols during any kinetic investigation of the system. Lack of this knowledge has been one of the factors that have hampered rigorous kinetic studies of the reaction.

The acid ionization constants have been determined at 25° C. for phenol and the hydroxymethylphenols (*13*); the temperature dependence of pK_a for phenol also has been determined (*2, 4*). Comparisons between our data and those reported previously are given below.

Our method involved the determination of the pH of aqueous solutions of very nearly 0.1*M* in each acid and an exactly equivalent amount of its sodium salt. The pK_a