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A STUDY OF THE PHASE BEHAVIOR OF THE ALUMINUM TRICHLORIDE-
ZIRCONIUM TETRACHLORIDE SYSTEM

A Thesis
Presented to
the Graduate Council of
The University of Tennessee

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

by
Arthur J. Shor
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CHAPTER I

INTRODUCTION

A. Objectives of Study

1. General Phase Behavior

The phase behavior of molten fluoride salts has received considerable attention in recent years as a result of their promising physical and chemical properties as nuclear reactor coolants. Chloride salts have received somewhat less attention. However, with the increasing interest in the latter as fast reactor coolants, as solvents in the reprocessing of spent reactor fuel elements by the chloride volatility technique, and as components of nuclear reactor blankets, research on chloride salt systems is accelerating. Part of this work involves the study of binary mixtures in which one or both of the components is an alkali or alkaline earth chloride. Relatively little effort has been allotted to mixtures of Group IIIA and Group IVB metal chlorides such as binary combinations of aluminum trichloride (AlCl_3) with titanium tetrachloride (TiCl_4), zirconium tetrachloride (ZrCl_4), or thorium tetrachloride (ThCl_4). These binary systems are especially interesting since the components do not exhibit the extensive ionic bonding of the alkali and alkaline earth halides, nor are they entirely covalent. They range from the rather predominantly ionic structures exhibited by thorium tetrachloride to the more covalent type structures of titanium tetrachloride and aluminum trichloride. In addition, the chloride anion in these melts is more polarizable than the fluoride ion adding to the complexities of the systems interactions. It is likely that

the cations do not have a simple structure in solution, but consist of associations or complexes of various kinds. There is considerable evidence for the existence of complex solid state crystalline structures for the pure salts. Aluminum trichloride is particularly interesting in that conductivity and x-ray measurements indicate that at the melting point a change from an ionic to a covalent structure occurs together with a large increase in the molar volume.^{1,2,3} Zirconium tetrachloride is believed by Blumenthal to exist as a hexachlorozirconate ion (ZrCl_6^-),⁴ while Olah states that the structure is a molecular crystal lattice of the tin tetraiodide (SnI_4) type.⁵ Little is known of the liquid structure of ZrCl_4 . Thus a phase study of the aluminum trichloride-zirconium tetrachloride binary could be significant in providing some insight into solid liquid structure and thermodynamic activities of the components.

2. Friedel-Crafts Catalysts

The importance of aluminum trichloride as a Friedel-Crafts catalyst is well known. Among the aluminum halides, it is outranked in catalytic activity by aluminum tribromide (AlBr_3) and even more so by aluminum triiodide (AlI_3). This effect is attributed to the decreasing energy requirements in obtaining the monomeric form which is believed to be the active form of the catalyst. However, the relative level of catalytic activity of aluminum trichloride, although significant in these reactions, is of less commercial importance than the excessive activity sometimes exhibited by aluminum trichloride which tends to catalyze undesirable side reactions. There is also an advantage in industrial processes in using a catalyst of not only uniform activity but of constant physical state, preferably the liquid state, since in this way the probability of poisoning or coating

the catalyst is diminished. Mixtures of aluminum trichloride and metal chlorides such as antimony trichloride (SbCl_3), titanium tetrachloride, or tin tetrachloride are active liquid catalysts which have been used in such applications. Solutions of aluminum trichloride in ethers, or ketones, or alcoholic solvents do not have sufficient catalytic activity.⁶ Since zirconium tetrachloride is considered a fairly good Friedel-Crafts catalyst, suitable combinations of aluminum trichloride and zirconium tetrachloride may offer useful properties in relation to catalytic activity and to the chemical and physical state of the catalyst. Furthermore, certain combinations of the two may increase the versatility of either catalyst so that a "tailor-made" mixed catalyst may be feasible.

3. Protactinium Recovery

A technique for the recovery of protactinium-233 (Pa^{233}), which is one of the products of neutron irradiated thorium tetrachloride, has been proposed which depends on the volatility and extractability of the protactinium-233 by aluminum trichloride. In this process a mixture of thorium tetrachloride and aluminum trichloride is irradiated, or a fluid stream of aluminum trichloride is passed over thorium tetrachloride irradiated in the blanket of a nuclear reactor. The aluminum trichloride leaves the melt, carrying with it protactinium-233 from the finely divided thorium tetrachloride. It is surmised that the effectiveness of the removal of protactinium depends on the solubility of thorium tetrachloride in aluminum trichloride. Since a saturated solution of thorium tetrachloride in aluminum trichloride in the temperature range of 200-400° contains less than 1 per cent thorium tetrachloride, methods of enhancing its solubility have been sought. Several physical and chemical properties of zirconium

tetrachloride, such as melting point and ionic nature on the Pauling electronegativity scale, are intermediate between thorium tetrachloride and aluminum trichloride. In addition, zirconium tetrachloride has a low cross section for the absorption of thermal neutrons. Thus the study of the binary mixtures of aluminum trichloride-thorium tetrachloride, thorium tetrachloride-zirconium tetrachloride, and aluminum trichloride-zirconium tetrachloride are indicated in that a ternary mixture may be suggested which would improve the practicability of the protactinium recovery process.⁷

It was for these objectives that the present study of the aluminum trichloride-zirconium tetrachloride system was undertaken.

B. Previous Investigations of Similar Systems

The system aluminum trichloride-titanium tetrachloride has been studied by I. S. Morozov and D. Y. Toptygen⁸ while B. G. Korshunov and co-workers⁹ have reported on the aluminum trichloride-thorium tetrachloride binary system. The solubility of aluminum trichloride in the low melting titanium tetrachloride is shown to be very low from -30° , the melting point of titanium tetrachloride, to approximately room temperature. Similar behavior is reported for the ferric trichloride (FeCl_3)-titanium tetrachloride system. The reverse situation is true for the aluminum trichloride-thorium tetrachloride system, in that very little thorium tetrachloride dissolves in the temperature range of the aluminum trichloride melting point, i.e., 193° up to 400° and higher. Solubility of aluminum trichloride in thorium tetrachloride at the melting point temperature of 760° is shown to be very small. Reports of the ferric trichloride-thorium tetrachloride system

indicate very similar behavior.⁸ Work on the aluminum trichloride-zirconium tetrachloride system, also by B. G. Korshunov,¹⁰ led them to postulate a broad liquid-liquid immiscibility region above 127° based on some rather sketchy and questionable data of melting of eutectic and monotectic mixtures. Liquidus data were not reported, apparently because of experimental difficulties related to the high vapor pressures developed by the binary at elevated temperatures. Thus their phase diagram is at least incomplete. On the other hand, I. S. Morozov and L. Tsegledi¹¹ report that the ferric trichloride-zirconium tetrachloride system gives a simple binary diagram with a eutectic at 14 mole per cent zirconium tetrachloride and 300°. The superficially similar aluminum trichloride (AlCl₃)-selenium tetrachloride (SeCl₄) system (melting point of selenium tetrachloride is about 305°, vapor pressure is one atmosphere at 170°) has been reported by H. Houtgraaf et al.¹² A 1:1 compound melting at 163.8° is shown with a eutectic at about 30 per cent aluminum trichloride. No region of liquid immiscibility was found. The selenium tetrachloride rich portion of the diagram is not reported, presumably due to the experimental difficulties with high vapor pressures. The same paper reports on the aluminum trichloride (AlCl₃)-tellurium tetrachloride (TeCl₄) system (melting point of tellurium tetrachloride is 227.9°) showing a 1:1 compound melting at 149.3°. The nitrosyl chloride (NOCl)-aluminum trichloride (AlCl₃) system was also studied by Houtgraaf. This system is particularly interesting because it shows a liquid-liquid immiscibility gap in the high AlCl₃ concentration region which extends from about 0.5 to about 10 per cent nitrosyl chloride. The immiscible phases were distinguishable in this system by the rather dark yellow-brown color of one liquid phase against a light yellow color for the aluminum trichloride rich liquid phase.¹³

The binaries of boron tribromide (BBr_3) with tin tetraiodide and tin tetrabromide (SnBr_4) might be mentioned,¹⁴ since boron is a homolog of aluminum, and the tetrahedral molecular crystal structure of tin tetraiodide is considered to be similar to that of zirconium tetrachloride. These binaries show eutectics close to the lower melting boron tribromide particularly with tin tetraiodide where the eutectic composition is only several mole per cent boron tribromide. I. N. Belyaev,¹⁵ in his extensive review of binaries forming two liquid phases, lists a single Group III and IV binary, that of antimony trichloride-tin tetrachloride. It is interesting that this system possesses a wide immiscibility region similar to that postulated by B. G. Korshunov et al. for the aluminum trichloride-zirconium tetrachloride system. In addition, a large number of systems involving aluminum trichloride and aluminum tribromide (AlBr_3) in association with Group I and II halides showing liquid-liquid immiscibility gaps of various widths are quoted in this review. These data are of particular interest in terms of the discussion of the aluminum trichloride-zirconium tetrachloride system which follows in that a number of properties of these systems such as liquid-liquid immiscibility and eutectic composition are similar to the results reported in this study.

CHAPTER II

MATERIALS, EQUIPMENT, AND EXPERIMENTAL TECHNIQUES

A. Materials Preparation

1. Aluminum Trichloride

Aluminum trichloride was prepared from the elements since efforts to achieve adequate purity by resublimation of reagent grade material from commercial sources were not successful. Procedures used were classical, in that high purity (99.99 per cent) aluminum metal powder was charged to a multisection quartz vessel and was reacted with carefully dried chlorine gas. The drying agent consisted of C.P. grade aluminum trichloride - the novel element in this preparation - thus minimizing contamination from the drying agent. The composition of the aluminum trichloride obtained by this method is shown in Table I. It should be emphasized that extreme precautions are necessary in this procedure due to the high vapor pressure of aluminum trichloride at elevated temperature and due to the exothermic formation reaction. No difficulty was experienced when using adequately designed vessels and maintaining the reaction temperature at about 200° (the triple point of aluminum trichloride is at 192.7° and a pressure of 171.5 cm.Hg as dimeric aluminum chloride).¹⁶ Since aluminum trichloride is extremely reactive, all handling was performed in a helium atmosphere dry box where the moisture was maintained at a level of 20-30 parts per million by volume.

Further checks on the purity of aluminum trichloride were made with the aid of emission spectrographic analysis, x-ray diffraction, and direct

thermal analyses. Table II shows a summary of the results of the spectrographic analyses. Since x-ray diffraction powder pattern techniques will only show gross impurities, such application was principally made later in the course of the research to determine possible compound formation of $\text{AlCl}_3 \cdot \text{ZrCl}_4$. Resublimed reagent grade aluminum trichloride showed evidence of the presence of the $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$. Aluminum trichloride derived from high purity aluminum metal showed a normal x-ray diffraction pattern. Melting points obtained by thermal analyses of the fresh material using calibrated chromel-alumel thermocouples and a Rubicon Type B High Precision Potentiometer were within $\pm 1^\circ$ of the triple point temperature. (Freezing point temperatures were depressed due to subcooling). Fresh material was prepared from time to time since the aluminum trichloride slowly deteriorated even when exposed to the dry box atmosphere.

2. Zirconium Tetrachloride

Material obtained by resublimation of reagent grade zirconium tetrachloride was generally found to be inadequate. Starting with so-called reactor grade material* and employing repeated sublimations, a material was obtained which was considered adequately free of sulfur, carbon compounds, and oxygen impurities. Table I and II list results from chemical and spectrochemical analyses. X-ray diffraction analysis did not show any additional lines in the powder pattern. Melting points were sharp both on heating and cooling and gave 437° and 438° , respectively, compared to a reported melting point temperature of $438 \pm 1^\circ$.¹⁷

*Supplied through the courtesy of U. S. Industrial Chemicals Company.

TABLE I
ANALYSIS OF CHLORIDE SALTS

	AlCl_3	ZrCl_4
Melting Point, °C		
Observed	192	437
Literature	192.7	438
Chemical Analysis, Wt %		
Cation		
Observed	20.31	39.16
Theoretical	20.23	39.14
Chloride		
Observed	79.60	58.3
Theoretical	79.77	60.86
H_2O		
Observed	0.27	0.07
Empirical Formula	$\text{AlCl}_{2.98}(\text{H}_2\text{O})_{0.02}$	$\text{ZrCl}_{3.83}(\text{H}_2\text{O})_{0.01}$

TABLE II
SPECTROCHEMICAL ANALYSIS OF CHLORIDE SALTS

Element	<u>Limit of Detection</u>		<u>Limit of Detection</u>	
	Wt %	<u>AlCl₃</u> Wt %	Wt %	<u>ZrCl₄</u> Wt %
Ag	0.002	—	0.002	—
Al	0.02	10-100	0.02	—
As	0.08	—	0.1	—
Au	0.004	—	0.005	—
B	0.005	—	0.01	—
Ba	0.2	—	0.2	—
Be	0.0001	—	0.00006	—
Bi	0.001	—	—	—
Ca	0.0001	—	0.0003	—
Cd	0.009	—	0.09	—
Co	0.0004	—	0.006	—
Cr	0.0002	—	0.005	—
Cu	—	0.00001-0.0001	—	0.0001-0.001
Fe	0.008	0.0001 -0.001	0.008	—
Ga	0.003	—	0.04	—
Ge	0.003	—	0.007	—
Hg	0.14	—	0.18	—
K	1.5	—	—	—
Li	0.01	—	0.5	—
Mg	—	0.0001 -0.001	—	—
Mn	0.0007	—	0.007	—
Mo	0.002	—	0.02	—
Nb	0.2	—	0.2	—
Na	0.04	—	—	—
Ni	0.0005	—	0.02	—
P	0.2	—	0.4	—
Pb	0.01	—	0.05	—
Pd	0.0003	—	—	—
Pt	0.02	—	0.03	—
Ru	0.003	—	0.4	—
Sb	0.01	—	0.02	—
Si	—	0.001 -0.01	—	0.001 -0.01
Sn	0.003	—	0.02	—
Sr	0.08	—	0.2	—
Te	0.09	—	0.1	—
Ti	0.002	—	—	—
Tl	0.12	—	—	—
V	0.001	—	0.02	—
W	0.09	—	0.7	—
Zn	0.02	—	—	—
Zr	0.007	—	—	10-100

B. Experimental Techniques

Many types of experimental equipment and techniques have been used for the study of the phase behavior of fused salts. Several of these were applied in this study — the principal one being differential thermal analysis (DTA). This method, which may be considered a refinement of thermal analysis, consists of comparing the temperature of the specimen under study with that of a suitably selected reference material of similar physical properties while both are heated simultaneously at a controlled and constant rate. For the purpose of determining melting points for the characterization of the pure components, the somewhat less sensitive but probably more accurate measurements by conventional thermal analysis were favored.

Where necessary, the study of some regions of the phase diagram was supplemented by direct visual observation of the disappearance of the solid phase. Due to the volatile nature of the salts, mixtures were sealed in quartz tubes of suitable design to withstand the vapor pressure generated. These were immersed in a transparent bath of a molten salt eutectic mixture. Direct viewing of liquidus points was particularly useful in the low to intermediate concentration region of zirconium tetrachloride.

To explore the possibility of compound formation, x-ray diffraction analysis was applied to a number of aluminum trichloride-zirconium tetrachloride mixtures at several elevated temperatures to detect any changes in phase or composition. Conventional x-ray powder patterns were obtained and analyzed.

1. Differential Thermal Analysis

The technique applied in this study was differential thermal analysis. This method has been used for a number of years in the earth sciences

and recently has received wider application in the study of fused salts. Review articles and books by Smothers and Chiang¹⁸ and W. Wendlandt¹⁹ are excellent sources. Generally the technique is to encapsulate a specimen and a physically similar and chemically inert reference substance. Both are placed in a relatively large heat conducting cylinder of stainless steel. The subassembly is symmetrically located inside a furnace which is heated at a constant rate. Any changes in phase causes a change in the heating rate of the specimen generating a temperature difference against the reference capsule. The differential temperature is recorded on an x-y plotter against either the temperature of the reference or the temperature of the specimen capsule. Whereas, curves obtained in conventional thermal analysis show the transition directly as a temperature halt, the analysis of curves obtained from differential thermal analysis in relation to the initiation or termination temperature of a transition is less direct. Since peaks have finite temperature widths, the help of the pure substances as references are useful in the determination of transition temperatures.

C. Experimental Equipment

The experimental equipment used in these studies was originally designed by T. B. Rhinehammer and co-workers.²⁰ Figure 1 is a photograph of the assembly. The furnace shown to the right is a 3 in. diameter, 12 in. long resistance heated, 1400 watt unit manufactured by the Hevi-Duty Electric Company. A model 9835-13 Leeds and Northrup D.C. microvolt amplifier is shown at the top of the instrument rack. This instrument is used to amplify the differential thermocouple signal providing increased sensitivity, and to prevent interaction in the x-y instrument by isolating the

Figure 1. Differential Thermal Analysis Equipment.

temperature thermocouples thus permitting the use of only two capsule thermocouples. See Figure 3 for the thermocouple circuit. The x-y plotter which records differential temperatures (horizontal) versus temperature (vertical) and the furnace temperature recorder are shown mounted beneath the amplifier. The programmer furnace controller is located in the lowermost section. Figure 2 shows the shell of the chamber which contains the experimental capsules. The top of this chamber can be seen just protruding from the furnace in Figure 1. On the left hand side of Figure 2 is shown the sealing flange which supports the 1.75 in. diameter cylindrical capsule block. A capsule centered with a magnesium silicate ring is shown inserted in a 0.5 in. hole in the block. When used with reactor materials of low volatility, the block is placed into the shell and the chamber may be either evacuated or supplied with a special atmosphere. Since the aluminum trichloride and zirconium tetrachloride salts are chemically active and very volatile at their melting points, evacuated and sealed nickel capsules designed to withstand very high pressures were used. A closeup photograph of these capsules as well as a quartz capsule used in direct visual studies is shown in Figure 4. A construction drawing for the nickel capsule showing welding details is shown in Figure 5. A diagrammatic representation of the entire apparatus is shown in Figure 3.

Nickel was selected for a capsule material as a result of tests which indicated good resistance to corrosion to the chloride salts at elevated temperatures. In addition, nickel possessed the strength to withstand the high pressures developed in these experiments. The capsules were designed for a working pressure of 2070 pounds per square inch at 427°C. However, it should be noted that the allowable pressure diminishes rapidly

Figure 2. Differential Thermal Analysis Capsules Holder and Shell.

Figure 3. Schematic of Differential Thermal Analysis Equipment.

Figure 4. Nickel and Quartz Specimen Capsules.

Figure 5. Construction Drawing of Nickel Capsule.

to about 850 pounds per square inch at 538° due to the rapid decrease in yield strength of nickel at elevated temperature. Allowance in the design was made for the presence and the nature of the welds. The thermocouple well was located along the axis of the cylinder and extended to about one-half the length of the salt column.

Sufficient material was charged to a capsule to minimize internal gas volume after melting so that composition changes were negligible. This required considerable free volume for aluminum trichloride rich mixtures due to the change in density of aluminum trichloride on melting from about 2.4 to 1.3 g./cm³. All transfers of material were performed in a special atmosphere dry box in a helium (He) atmosphere with moisture maintained between 20-30 parts per million by volume. The capsule filling tube was heliarc welded while mechanically sealed insuring the integrity of the sample. Similar treatment was afforded the aluminum oxide (Al₂O₃) reference capsule.

In performing an experiment, the usual procedure was to place the reference capsule and specimen capsule in the cylindrical block. Calibrated stainless steel sheathed, chromel-alumel thermocouples were then inserted and secured in the capsule wells and the block was placed into the furnace chamber. The thermocouple network was plugged into the amplifier-plotter units, and the furnace programmer was adjusted for the rate of heatup and cooldown desired, generally, 1 to 2°/min., the former being the lowest rate available. Additional adjustments for maximum operating temperature and for length of time at maximum temperature or "soak" time were also made at this time. The "soak" temperature which was held for four hours was selected to exceed the liquidus temperature by about 50°.

If the run represented an original heatup of the mixture, an eight-hour halt at maximum temperature was programmed. Invariably, the first run was discarded. A number of heatups were made, both for equilibration purposes and to determine reproducibility for any given cycle. Prior to startup the "y" or temperature axis of the x-y plotter was calibrated with a Precision Leeds and Northrup Potentiometer. The "x" axis on which the differential signal was plotted was checked less frequently. A second check on the "y" calibration was often made following a run to ensure freedom from drift over the approximately twenty-four hour running period.

D. Interpretation of Differential Thermal Analysis Curves

Figure 6 shows a representative selection of differential thermal analysis heating curves recorded at several different compositions of aluminum trichloride-zirconium tetrachloride mixtures. Differential temperature is shown plotted in the vertical direction versus the temperature of the aluminum oxide reference. The practice of plotting the reference temperature rather than the specimen temperature along one axis was preferred in these studies since comparisons with other work in the literature is facilitated, and since it was found that more consistent and interpretable data were obtained.

When the melting of a pure substance occurs, the differential thermal analysis curve starts to deviate from the flat baseline while the difference in temperature of the specimen increases as in Curve a in Figure 6. The graph rises at a rate related to the rate of heating and the physical properties of the material. When the pure sample is finally melted, the

Figure 6. Differential Thermal Analysis Heatup Curves.

specimen capsule temperature "catches up" to the reference temperature and the curve returns to the horizontal baseline.

In the case of simple mixtures, a peak is first obtained which represents the melting of the eutectic mixture. Since melting continues to occur after passing the eutectic temperature, the curve does not return to the baseline until all solids has melted. This may be seen as a second peak or as an abrupt change in slope of the differential thermal analysis curve as in Curves b and c in Figure 6.

Smyth²¹ has attempted a theoretical analysis of a differential thermal analysis system to determine the significance of the various portions of the differential temperature versus temperature curves. He computed the shape of the peaks by analyzing a mathematical model consisting of a thin slab of material subjected to a linear heating cycle while undergoing an endothermic reaction. For thermocouples symmetrically located in the material, the temperature at the apex of the differential temperature versus temperature curve indicated the transition temperature of the specimen if the differential temperature was plotted against the specimen temperature. If the differential temperature was plotted against the reference temperature, the transition temperature for the endothermal peak occurred on the curve, between the horizontal baseline, which is traced during the steady state period of the run, and the apex.

It was further suggested by Schraid²² that if the heating rate is sufficiently slow to produce a straight-line portion during an endothermic reaction, the extrapolation of this line to the baseline will give a good measure of the transition temperature. It was found in this study that such a procedure gives values for the melting point of the pure substances

which most closely and consistently correspond to accepted values. However, small corrections to the transition temperature were necessary in practice since situations which only approximate reality are used in developing the mathematical models. National Bureau of Standards lead was used as a standardization material in addition to lithium chloride (LiCl) and sodium chloride (NaCl). These samples gave temperature halts when using conventional thermal analysis, which were within $\pm 1^\circ$ of the accepted values.

As seen in Figure 4, some curvature was encountered on the rise of the curve obtained in the analysis for mixtures. In this case the slope of the leading edge of the curve at its inflection point was used for purposes of back extrapolation. Curve c in Figure 6 shows a liquidus transition following a eutectic melting. In this case, the differential temperature does not return to the baseline after the initial melting, as with a pure substance, but continues a gradual return depending on the shape of the liquidus line of the phase diagram. The curve shows a discontinuity in slope when all the solid is consumed. The liquidus temperature is taken close to this break. This interpretation was confirmed by comparing the more abrupt changes on freezing in cases where supercooling did not occur. However, it should be emphasized that generally cooling curves were not useful in this study for purposes of discovering transition temperatures, particularly in the aluminum trichloride rich section of the phase diagram. At high zirconium tetrachloride concentrations and for pure zirconium tetrachloride, liquidus transitions for both heating and cooling were reproducible within 1 to 2 degrees. The supercooling occurring in the aluminum trichloride rich section is discussed in more detail below in relation to the interpretation of studies by Korshunov¹⁰ on the aluminum trichloride-zirconium tetrachloride system.

Curve b in Figure 6 shows a differential thermal analysis curve with a double peak. Such shapes were obtained in a part of the aluminum trichloride rich section of the phase diagram. The second peak represented, as will be discussed below in conjunction with the phase diagram, a change from pure zirconium tetrachloride in equilibrium with liquid solution to an equilibrium with a two phase liquid mixture. Thus the second peak represented an abrupt change between a rather low rate of energy absorption to a high rate, both resulting from the melting of zirconium tetrachloride. The apex of the second peak was interpreted as the temperature of the monotectic transition. Attempts to observe these transitions by direct visual methods generally gave scattered and rather high results averaging about 5° above the temperatures represented by the second peak. These are discussed below in the section on experimental observations.

E. Supplementary Experimental Techniques

1. Thermal Analysis

In order to standardize observations of transition temperatures made by differential thermal analysis, it was necessary to determine melting points of the pure components by an alternate method. Although differential thermal analysis is a more sensitive means of detecting transition temperatures, the relative lack of ambiguity in conventional thermal analysis was a factor in using such procedures for standardization.

The pure components were loaded into nickel capsules identical to those described for differential thermal analysis observations and these were placed into a cylindrical furnace similar to that described above. Calibrated chromel-alumel thermocouples were read with a Rubicon Type B

High Precision Potentiometer. Readings of temperature versus time were also recorded continuously with a suppressed zero recorder having a 3 mv. range over a 10 in. scale. Heatup rates were about $1^{\circ}/\text{min}$. The potentiometer was read every minute when going through a transition. These points were subsequently graphed manually. The latter method gave very satisfactory temperature halts which compared well with literature values. Lithium chloride, sodium chloride, as well as aluminum trichloride, zirconium tetrachloride, and thorium tetrachloride, were studied in this manner. A standard sample of lead from the National Bureau of Standards, melting point 327.40° , was also used for the calibration of the differential thermal analysis apparatus.

2. Direct Visual Methods

Since very high vapor pressures developed in these salt mixtures, the application of direct visual methods were necessarily limited. The quartz capsules shown in Figure 4 which were similar in size to the nickel capsules used for the differential thermal analysis tests were capable of withstanding temperatures and pressures corresponding to aluminum trichloride heated to 250° or about 10 atmospheres. Capillary tubes measuring 5 mm. outside diameter and 1 mm. wall thickness easily withstood pressures in the region of the aluminum trichloride critical temperature or about 29 atmospheres at 350° and were thus useful for the higher temperature ranges. The tubes were immersed in a lithium nitrate (LiNO_3), sodium nitrate (NaNO_3), potassium nitrate (KNO_3) eutectic contained in a 1 liter beaker.* The melt was very transparent and practically colorless, remaining

* Convenient quantities for a one liter bath are: 404 g. LiNO_3 , 189 g. NaNO_3 , and 752 g. KNO_3 . The density of the melt ranges from 2.4 to 2.25 g./cm^3 .²³

molten to below 150° . The bath was stirred with a stainless steel stirrer and heated with a hotplate and an immersion heater. Glass wool insulation surrounding the beaker was required to reach higher temperatures. After some experience with this arrangement, it was possible using variable transformers to adjust the power input to give a reasonably slow and constant temperature rise. The capsules were tied to glass rods which were supported overhead. Chromel-alumel thermocouples enclosed in 310 stainless steel sheaths were used to measure temperature. Mercury thermometers were not useful since attack by the salt was sufficient to quickly alter the calibration. Temperature gradients, with even a low rate of stirring, at reasonable distances from the heaters were negligible. The capsules were shaken frequently and occasionally removed from the bath and quickly upended and returned. Very good agitation was thus attained. The highest temperature attempted in this setup was 380° which is the critical temperature of a 14 mole per cent mixture of zirconium tetrachloride and aluminum trichloride.

CHAPTER III

DISCUSSION OF EXPERIMENTAL RESULTS

A. General Phase Behavior

Figure 7 shows the solid-liquid binary phase diagram of the aluminum trichloride-zirconium tetrachloride system throughout the range of composition. A magnified portion of the system in the low zirconium tetrachloride concentration range is shown in Figure 8. The data are plotted as temperature in °C versus mole percentage of zirconium tetrachloride. For the sake of simplicity, monomeric aluminum trichloride is used as a basis for graphing. The open circles on the diagrams represent information derived from differential thermal analysis experiments while the solid circles are data obtained by the direct viewing of melting in quartz capsules. It was necessary to use visual observations in the 10 to 25 per cent zirconium tetrachloride region of the diagram because the very small changes in curvature of the differential thermal analysis trace due to the steepness of the liquidus curve in this range rendered precise interpretation difficult. The smooth merging of the liquidus data from the differential thermal analysis observations and those by visual observations may be noted on the diagram. Direct visual observations of eutectic and monotectic temperatures on heating were obscure and difficult to reproduce. Differential thermal analysis data was shown for those transitions. Data obtained on cooling are shown as solid squares. Supercooling effects on the freezing point of the eutectic mixture are readily apparent. At zirconium tetrachloride concentrations greater than ~33 per cent, supercooling of the liquidus transition was

Figure 7. Binary Phase Diagram, Aluminum Trichloride-Zirconium Tetrachloride System.

Figure 8. Aluminum Trichloride Rich End of the Aluminum Trichloride-Zirconium Tetrachloride Binary Phase Diagram.

relatively small. Throughout the entire range of concentrations supercooling of the monotectic and eutectic compositions ranged from 10 to 50°.

Data obtained by B. G. Korchunov et al.¹⁰ for the aluminum trichloride-zirconium tetrachloride system are shown in Figure 8 as crosses. These were obtained for a limited region of the phase diagram and parallel data which represent supercooled freezing temperatures of the binary liquid mixtures.

In Figure 7 in the region of ~10 to 100 mole per cent zirconium tetrachloride, complete miscibility of the liquid mixture is postulated, while in the region of ~3 to 10 mole per cent zirconium tetrachloride a narrow two phase section is shown with a monotectic composition of 10 per cent zirconium tetrachloride at 192°. An aluminum trichloride-zirconium tetrachloride eutectic is evident at 2.5 per cent zirconium tetrachloride and 170°. The occurrence of a monotectic and eutectic separated by only ~22° results in a narrow temperature range where pure zirconium tetrachloride is in equilibrium with liquid 1. At temperatures directly above this band, zirconium tetrachloride is in equilibrium with liquid 2. Attempts to determine the limits of the region of immiscibility as a function of temperature or the upper critical solution temperature by differential thermal analysis and direct observation were unsuccessful. Resolution of the eutectic and liquidus transitions was not possible on the aluminum trichloride rich side of the eutectic composition either by differential thermal analysis or direct visual observation. The possibility for solid solution in this region is not excluded. The open circles indicate the transition temperatures by differential thermal analysis which are here interpreted as liquidus transitions.

The melting point temperatures of the pure substances were measured within an error of $\pm 1^\circ$. However, as described above in the section on interpretation of differential thermal analysis curves, the precision of liquidus and eutectic temperature measurements was somewhat less. The latter observations as well as liquidus temperature measurements made by direct visual observation probably were reliable within $\pm 3^\circ$.

Table III is a listing of the data from which the curves are derived together with notes on the observations.

B. Activity Coefficients of Zirconium Tetrachloride

Activities were calculated from the liquidus curve in the zirconium tetrachloride rich portion of the diagram. It was assumed that no solid solution of aluminum trichloride in zirconium tetrachloride occurred, that the difference in heat capacity between pure solid and supercooled liquid was negligible and that the heat of fusion was constant, so that the following relation was applicable.²⁴

$$\ln a_{\text{ZrCl}_4} = \frac{\Delta H_{\text{ZrCl}_4}}{R} \left(\frac{1}{T_o} - \frac{1}{T_m} \right)$$

where

a_{ZrCl_4} is the activity of the zirconium tetrachloride referred to the pure supercooled liquid zirconium tetrachloride,

ΔH_{ZrCl_4} is the heat of fusion of pure zirconium tetrachloride, 9.0 ± 0.9 kilocalorie per mole,²⁵

T_m and T_o are the melting temperatures of the mixture and pure zirconium tetrachloride, respectively,

R is the gas constant.

TABLE III
MELTING AND FREEZING POINT TEMPERATURES OF THE ZIRCONIUM TETRACHLORIDE-
ALUMINUM TRICHLORIDE BINARY PHASE SYSTEM

Composition Mole Per cent ZrCl_4	Transition Temperatures on Heatup, °C			Transition Temperatures on Cooldown, °C	
	I	II	Liquidus	I and II	Liquidus
100	—	—	437	—	435
90	167	191	425	150 (a)	420
80	159	—	419	144	417
75	160	—	—	139	396
67	163	—	399	144	396
50	162	—	369	143	366
40	166	—	350	154 (a)	—
33	168	191 (c)	320 (a)	150	317
25	164	198	312 (b)	135	262
20	167	193	291 (b)	130	234
14	163	192	245 (b)	125	—
10	170	192	194 (b)	120	—
7	170	187 (c)	—	125	—
5	172	188 (c)	—	127	—
4	171	190 (c)	—	132	—
3	178	188 (c)	—	135	—
2	183	—	—	160	—
1	185	—	—	162	—
100 per cent AlCl_3	193	—	—	183	—

(a) Vague transition

(b) By direct visual observation

(c) Poor resolution of second peak

Activities were calculated for the various liquidus temperatures in the temperature range from the melting point of zirconium tetrachloride at 437° to 250° . The activities were then compared to the corresponding mole fraction of zirconium tetrachloride expressed in two ways: first, as a mixture with dimeric aluminum chloride and second, as a monomeric aluminum trichloride mixture. These data are listed in Table IV together with the corresponding activity coefficients. Also shown are excess free energies expressed as $-RT \ln \gamma$ for the mixture with dimeric aluminum trichloride.

From the table and by referring to Figure 9 showing a plot of activity versus mole fraction of zirconium tetrachloride, it may be seen that a solution of the dimer in zirconium tetrachloride is apparently far from ideal. On the other hand, the activities of zirconium tetrachloride as a simple molecule versus mole fractions of zirconium tetrachloride in a mixture with monomeric aluminum trichloride fall close to the 45° line, thereby suggesting an activity coefficient of unity over the range of concentrations shown.

A test of the "regular solution"²⁶ character of the dimeric aluminum trichloride mixture was made by comparing the calculated apparent excess free energy $-RT \ln \gamma$ with the square of the mole fraction of dimeric aluminum trichloride in the mixture. A linear relationship should hold over a reasonable range of concentration. It was found that there was considerable curvature after a dimeric concentration of 14 per cent, suggesting that the dimeric aluminum trichloride hypothesis does not correspond to the regular solution concept as adequately as the monomeric aluminum trichloride hypothesis corresponds to the ideal solution model.

TABLE IV
ACTIVITIES OF ZIRCONIUM TETRACHLORIDE

Melting Point °C.	Computed Activity ZrCl ₄	Composition Mole Fraction ZrCl ₄ + AlCl ₃	γ_{ZrCl_4} in monomer	Composition Mole Fraction ZrCl ₄ + Al ₂ Cl ₆	γ_{ZrCl_4} in dimer	Excess Partial Molar Free Energy (cal) dimer (-RT ln γ)
437	1	1	1	1	1	0
425	0.89	0.90	1.0	0.95	0.9	86
419	0.84	0.80	1.1	0.89	0.9	71
399	0.70	0.67	1.1	0.80	0.9	170
369	0.51	0.50	1.0	0.67	0.8	350
350	0.41	0.40	1.0	0.57	0.7	410
320	0.29	0.33	(0.9) ^a	0.50	(0.6) ^a	(650) ^a
312	0.26	0.25	1.0	0.40	0.7	500
291	0.20	0.20	1.0	0.33	0.6	580
245	0.10	0.14	0.7	0.25	0.4	920

^a Value uncertain; in general based on temperature and heat of fusion measurement limitations the uncertainty in the activity coefficients is estimated to be ± 10 percent.

Figure 9. Activities of Zirconium Tetrachloride in Monomeric and Dimeric Aluminum Trichloride.

The apparent ideal behavior of the monomeric model may be fortuitous since considerable energy must be supplied for the reaction.

The energy for this reaction in the gaseous state is 29.6 kilocalories per mole. However, molecular weight determinations in a number of solutions have indicated a correspondence with the monomeric formula. This generally occurs in coordinating solvents such as ether which supply enough interaction energy from the solution process.²⁷ It is problematical that reaction with the zirconium tetrachloride solvent which tends like aluminum trichloride to be an electron acceptor and forms adducts with oxygen donors and halides would be energetic enough to supply the requirements of this reaction. However, assuming the existence of the monomer above concentrations of 10 per cent zirconium tetrachloride and the stability of the dimer at very high aluminum trichloride concentrations, i.e., greater than about 97 per cent, it is conceivable that an equilibrium between these two states is evidenced by the apparent liquid immiscibility in this region of the phase diagram discussed below.

C. The Aluminum Trichloride Rich Region

The aluminum trichloride rich section of the phase diagram was intensively investigated to determine if the double transition observed in the greater than 3 per cent zirconium tetrachloride region was the result of the formation of a compound or involved a region of two liquid phases. In addition, since differential thermal analysis techniques occasionally produce spurious temperature responses, the possibility that the higher

temperature transition was an artifact was not excluded. By varying the shape, the loading, and the position of the specimen capsule in the differential thermal analysis apparatus in an attempt to alter or eliminate this effect, it was determined that the temperature transitions were reproducible despite these mechanical changes in the experimental procedure. Several compositions showing distinctly resolvable and intense double peaks corresponding to the eutectic and monotectic transition temperatures at 10 and 20 per cent zirconium tetrachloride were analyzed by x-ray diffraction methods at temperatures close to the first transition temperature, 170° . Powder patterns indicated changes which could not be interpreted as the formation of an aluminum trichloride-zirconium tetrachloride compound, but merely indicated that incipient melting was occurring. X-ray diffraction analyses at lower temperatures, close to a transition region and at room temperature, indicated the presence of pure aluminum trichloride and zirconium tetrachloride. No additional lines indicating compound formation were found.

Direct viewing of the melting process and the molten mixture in various size capsules and with different degrees of lighting did not show any phase separation. However, color changes were observed similar to those noted by Houtgraaf as discussed below. Presumably as a result of the similarity in composition of the two liquid phases, there was insufficient difference in their indexes of refraction to show any interface or cloudiness upon the formation of the two liquid phases.

J. Kendall and E. D. Crittenden,²⁸ and more recently, I. N. Belyaev¹⁵ discussed a large number of binary systems involving aluminum tribromide or aluminum trichloride with various chloride salts. In many cases, liquid

separation was noted in the 80 to 100 mole per cent aluminum trichloride or aluminum tribromide region of the phase diagram. It was pointed out by Belyaev that if the second compound was polar, the two-liquid region consisted of an equilibrium between aluminum trichloride and a complex compound of the two salts. If both salts were nonpolar or if the complex was unstable in the liquid state, two liquid phases of the simple compounds occurred.

Houtgraaf and De Roos¹³ in their study of the binary system nitrosyl chloride (melting point, 61°) with aluminum trichloride found a narrow immiscibility region from about 84 mole per cent aluminum trichloride to about 99 per cent, at 195° . They speculated that the large difference in cohesive energy between the molecules of a partly ionic addition compound $[\text{NO}]^{+}[\text{AlCl}_4]^{-}$ in the liquid state and the molecular liquid of dimeric aluminum trichloride could lead to such an immiscibility region. However, the authors stated that the extremely eccentric position of the region could not be explained in this way, but would require a liquid addition compound of the molecular formula $[\text{NO}]^{+}[\text{Al}_5\text{Cl}_{16}]^{-}$ of which they found no indication in the solid state. They were able to visually and unambiguously distinguish between the two phases since the aluminum trichloride rich phase was light yellow while the nitrosyl chloride rich phase was greyish brown. Thus in all of these cases, narrow regions of immiscibility in the aluminum-halide rich side of the binary, similar to that shown in Figure 8 for the aluminum trichloride-zirconium tetrachloride system, were observed or inferred in the studies reported. It is apparent from the shape of the zirconium tetrachloride liquidus curve that the extent of the immiscibility region is limited to below 10 mole per cent zirconium tetrachloride. The

eutectic composition which appears to lie at 2 to 3 mole per cent zirconium tetrachloride forms the lower composition limit for the two phase region. Thus a narrow band of immiscibility between about 4 and 10 mole per cent zirconium tetrachloride is postulated.

Calculations were made of the critical composition and critical solution temperature for liquid-liquid immiscibility expected in this system by the regular solution - solubility parameter theory.²⁹ The molar volume of liquid zirconium tetrachloride was assumed to be the same as the solid due to the lack of data on liquid densities, and both monomeric and dimeric forms of aluminum trichloride were considered. It was found that predictions from the regular solution theory differed markedly from the critical composition estimated from the data. The predicted critical solution temperatures were below room temperature. Evidently differences in cohesive energy density (essentially the square root of the molar energy of vaporization divided by the molar volume) of the monomeric or the dimeric forms of aluminum trichloride versus zirconium tetrachloride are insufficiently great to account for liquid-liquid immiscibility. This would suggest that other types of liquid associations could exist rather than the simple monomeric-dimeric aluminum trichloride-zirconium tetrachloride model used in the calculation. It is interesting that in Belyaev's review mentioned above the solid phase in equilibrium with the two liquid phases generally consisted of a compound of aluminum trichloride or aluminum tribromide and the second salt. Although the existence of a simple compound as pointed out by Houtgraaf and De Roos would not be sufficient to account for the very eccentric position of the immiscibility gap, more complex liquid addition compounds might exist in the aluminum trichloride rich phase. These

would be in equilibrium with an essentially monomeric aluminum trichloride-zirconium tetrachloride solution as evidenced by the activity coefficient measurements mentioned above in the zirconium tetrachloride rich section of the phase diagram and perhaps account for the liquid-liquid immiscibility.

D. The Eutectic Region

Based on the first transition at 170° which was observed almost throughout the range of compositions, and based on the trend of the melting point data, it is estimated that the binary system forms a simple eutectic between 2 and 3 per cent zirconium tetrachloride. However, below 3 per cent zirconium tetrachloride no eutectic melting was observed. Since data taken in the narrow region of 0-3 per cent zirconium tetrachloride in a temperature range of between 170 - 190° approaches the experimental limitations of the visual and differential thermal analysis techniques used in these studies, it is not clear that the absence of data is evidence for the existence of a region of solid solution. Consideration of the relative sizes of the simple cations in this binary does not shed light on this question, since it is known that aluminum trichloride in the solid state has a complex ionic-like structure while zirconium tetrachloride is thought to have a tetrahedral molecular crystal structure. The aluminum trichloride lattice is considered to be decidedly labile, as attested by the low sublimation temperature of 183° , and it is presumably highly deformable; so that the transformation to the less polar bonding of the dimeric form does not require the expenditure of a large quantity of energy. The association of zirconium tetrachloride molecules through formation of complex ions occurs to an appreciable extent in the liquid state with the formation of

hexachlorozirconate ions (ZrCl_6^-). Similar hexachloroaluminate ion structures have been suggested for crystalline aluminum trichloride. It is therefore likely that an appreciable degree of solid solution is present in the region below the eutectic composition.

E. Supercooling Effects

Considerable supercooling of the eutectic transition occurred throughout the range of compositions when cooling even at rates as low as $1^\circ/\text{min}$. The amount of supercooling varied between 10 to 15° , depending roughly on composition. As may be seen from Figure 7, the greatest differences occurred close to the monotectic composition at about 10 mole per cent zirconium tetrachloride. The freezing temperatures were reproducible to $\pm 5^\circ$. The metastability observed was probably not related to the rate of crystallization since the subcooled liquid was quite stable for extended periods at temperatures slightly above the freezing point and precipitated very rapidly following a further decrease in temperature. Although it may appear at first glance that the high degree of supercooling is related to the partial covalent nature of the components, it was observed that pure thorium tetrachloride which is apparently more ionic than zirconium tetrachloride shows very striking supercooling effects, freezing at temperatures of about 720° compared to a melting temperature of 760° .⁷ Similar effects have been reported for aluminum trichloride-titanium tetrachloride mixtures.³⁰

Very little supercooling was noted in the measurements of the liquidus temperatures in the high zirconium tetrachloride section of the phase diagrams. Below about 33 per cent zirconium tetrachloride, either

due to supercooling or to the steepness of the liquidus curve, no clear transitions were observable by differential thermal analysis techniques. It is noteworthy that considerable supercooling of the monotectic and eutectic occurred even in the presence of relatively large quantities of the solid zirconium tetrachloride phase. This phenomenon has been termed two-phase undercooling by W. M. Smit³¹ while the more usual single phase variety is termed monophasic undercooling. The latter, according to Smit, depends on rate of nucleus formation whereas in the two-phase undercooling situation, the extent of supercooling is more related to rate of crystal growth. However, visual observation of aluminum trichloride-zirconium tetrachloride melts over periods of days indicated no crystal growth, so that crystal-growth rates were evidently very slow or not significant in the so-called two-phase undercooling at temperatures only slightly above the freezing point.

Although it is not clearly stated by B. G. Korchunov and co-workers¹⁰ in their study of the aluminum trichloride-zirconium tetrachloride system whether their data were obtained from melting or freezing experiments, it appears that they report freezing data only. Figure 8 showing this data as crosses indicates a remarkable correspondence with the data on subcooled temperatures. Except for a single point at 36 per cent zirconium tetrachloride, four pairs of points are shown. It is believed that these double points are an artifact and result from incomplete coverage of the thermocouple by the melt in the Korchunov experiments. Similar effects were obtained in this study when checking the significance of thermocouple location. With the thermocouples located in a well at the top of the capsule, it was found that on heating the usual transitions

were observed. On cooling, presumably as a result of the large density changes and the falling down of the solids, the thermocouple was exposed to several temperature interruptions during the freezing process. This situation may have existed in the work reported by Korchunov and co-workers. It is not understood, however, why these workers did not consider heatup data significant enough to report.

CHAPTER IV

SUMMARY AND CONCLUSIONS

1. General Phase Behavior

The aluminum trichloride-zirconium tetrachloride binary system has been studied through the complete range of compositions using differential, thermal and visual analysis of melting and freezing phenomena. It was found that from about 33 to 100 mole per cent zirconium tetrachloride, the zirconium tetrachloride liquidus curve displayed nearly ideal behavior based on the model of a solution of monomeric aluminum trichloride in zirconium tetrachloride. In the lower than 33 per cent zirconium tetrachloride region, the results indicate a monotectic at 192° consisting of an equilibrium of solid zirconium tetrachloride with two liquid solution phases. The narrow liquid-liquid immiscibility region appeared to extend from 4 to 10 per cent zirconium tetrachloride. An eutectic at 2-3 per cent zirconium tetrachloride was formed at 170° while below this concentration some degree of solution of zirconium tetrachloride in solid aluminum trichloride may have occurred. Considerable subcooling was noted for eutectic and monotectic transition temperatures so that most of the information reported is based on heating rather than cooling data. No evidence of compound formation was shown by x-ray diffraction analysis at a number of temperatures and compositions.

The phase diagram obtained appears to be consistent with trends of data reported in other investigations of binary systems containing aluminum trichloride. For example, the presence of a eutectic of high percentage aluminum trichloride, the sharp initial rise of the liquidus curve, and the

presence of two liquid phases appear to be characteristic of a number of such systems.^{13,15}

Previous work by Morozov et al.¹⁰ on a portion of the aluminum trichloride-zirconium tetrachloride system appears to be faulty. Apparently these workers used data based on cooling curves. It has been shown that in this system a considerable difference exists between heating and cooling data due to supercooling.

2. Friedel-Crafts Catalysts

Since aluminum trichloride appears to exist as the monomer in the liquids, at least at concentrations of 90 per cent and lower, such mixtures should show good catalytic activity and could be useful as Friedel-Crafts catalysts, if their high vapor pressures are tolerable. At concentrations higher than 90 per cent aluminum trichloride where two liquid phases appear to exist, the form of aluminum trichloride in the aluminum trichloride rich liquid phase is in doubt. As a result of the monotectic at 192°, no appreciable lowering of the gross melting point of zirconium tetrachloride-aluminum trichloride mixtures and probably no significant lowering of the vapor pressure of the liquid melt is achieved. However, the very stable and reproducible subcooling phenomena observed which was maintained even in the presence of solid, precipitated zirconium tetrachloride, may have application. The full range of compositions for the formulation of "tailor-made" catalysts may thus be made available at temperatures 10 to 50° below the eutectic temperatures of 172° with undoubtedly reduced vapor pressures. Such supercooled compositions may have commercial significance. However, it will first be necessary to study the stability of the solutions while participating in a Friedel-Crafts reaction.

3. Protactinium Recovery

The use of zirconium tetrachloride as a "bridging solvent" between the aluminum trichloride and thorium tetrachloride was investigated by studying the three binaries involved. In the temperature range of interest, 200-350°, which is considered suitable for a process for the removal of protactinium from neutron irradiated thorium tetrachloride, the solubility of thorium tetrachloride in aluminum trichloride was found to be less than 1 per cent while the solubility of zirconium tetrachloride in aluminum trichloride was found in the present study to range from 10 to 40 mole per cent. However, the investigation of several zirconium tetrachloride-thorium tetrachloride mixtures indicated very little change in the melting temperature of zirconium tetrachloride. The evidence from the study of the three simple binaries of the aluminum trichloride-zirconium tetrachloride-thorium tetrachloride system suggests that the possibility of finding a homogeneous ternary composition of appreciable thorium tetrachloride concentration is remote.

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