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Oxidation states of thorium in fused LiCl-KCl eutectic

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OXIDATION STATES OF THORIUM IN FUSED LiCl-KCl EUTECTIC

by

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In Charge of Major Work

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INTRODUCTION

Until recently there had not been much work done on the lower halides of thorium. Until about 1957 only a few authors had discussed the possibility of forming these lower halides. In 1949, Anderson and D' Eye (1) succeeded in preparing the di- and tri-iodide of thorium by reduction of the tetraiodide with metallic thorium. At about this same time, Hayek, Rehner, and Frank (2) succeeded in preparing the di- and tri-iodides, bromides, and chlorides of thorium. According to their work, the trihalides were prepared by reduction of the tetrahalide with metallic thorium at temperatures of 500, 570, and 620°C. for the iodide, bromide, and chloride respectively.

These trihalides were found to disproportionate to the tetra- and dihalides:

$$2ThX_3 \rightarrow ThX_4 + ThX_2. \tag{1}$$
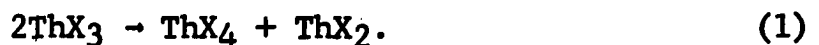
The disproportionation temperatures for this reaction were found to be 550, 595, and 630°C. for the iodide, bromide, and chloride respectively.

The dihalides were found in turn to disproportionate at higher temperatures to the tetrahalide plus metallic thorium:

$$2ThX_2 \rightarrow ThX_4 + Th. \tag{2}$$

The disproportionation temperatures for this reaction were found to be 600, 640, and 670°C. for the di-iodide, bromide, and chloride respectively. Corbett and Clark (3) in 1963 also prepared ThI_2 and obtained evidence for the tri-iodide.

Outside of the work done by Anderson and D'Eye and by Hayek et al. not much work was done on the lower halides of thorium prior to the later 1950's. This was undoubtedly due to the fact that the chemistry of the early 1950's was concerned chiefly with aqueous chemistry. Since lower halides of thorium are expected to be unstable in this media, it is not surprising that very little information was obtained concerning these lower valent compounds.

More recently, however, a tremendous amount of research has been done in fused salt media, particularly in the fused alkali metal halides. One of the most popular of these solvents has been LiCl-KCl eutectic (44.4 wt.% LiCl). This solvent is especially attractive due to its low melting point (355°C.) and its great stability with respect to other metal chlorides. Since this solvent is exceedingly stable, it can support metal chlorides which would be unstable in aqueous media. With this possibility, the question as to which oxidation states of thorium exist in this fused salt media has

come to the fore.

Inman, Bockris et al. (4) found upon anodic dissolution of thorium into the eutectic melt, a value of 3.7 to 4.5 for n, the number of electrons given up per gram atom of thorium dissolved into the salt. Gruen et al. (5), in their review of the chemistry of the actinide elements in the fused LiCl-KCl eutectic, interpreted this work by Inman as indicating that only the plus four oxidation state of thorium exists in these solutions. To support this thinking, they dissolved one gram of $ThCl_4$ in ten grams of LiCl-KCl eutectic contained in a single-crystal sapphire crucible and placed a piece of thorium metal in contact with the melt at 500^OC. for four hours. They found no change in the weight of the thorium metal indicating that no reaction between the tetrachloride and the metal had occurred. In direct contradiction to these data, however, Smirnov and Ivanovskii (6) claimed that in the temperature range of $510-897^O$C., an equilibrium between $ThCl_4$ and $ThCl_2$ was occurring in the fused LiCl-KCl eutectic:

$$Th + ThCl_4 \rightleftharpoons 2ThCl_2. \tag{3}$$

In addition to these conflicting data, Parry and Chiotti (7), in their study of the oxidation and reduction of thorium in the two phase, LiCl-KCl eutectic-liquid zinc system,

obtained data which indicated that perhaps an equilibrium between the tetra and trichlorides was occurring in the system:

$$3ThCl_4 + \tfrac{1}{2}Th_2Zn_{17} \rightleftharpoons 4ThCl_3 + 8.5Zn. \tag{4}$$
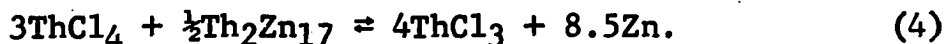
It was with these conflicting pieces of data in mind that this investigation was undertaken.

The object of this research was to prepare, if possible, the lower chlorides of thorium, $ThCl_3$ and $ThCl_2$, and to determine the oxidation states of thorium in LiCl-KCl eutectic when in equilibrium with thorium-zinc alloys. Toward this end, a partial investigation of the Th-ThCl$_4$ phase diagram was carried out; the activity of $ThCl_4$ in the salt as a function of temperature and composition was investigated; the e.m.f. of the cell Th/LiCl-KCl-ThCl$_x$/Th$_2$Zn$_{17}$(s), Zn(l) as a function of temperature and ThCl$_x$ content was measured; batch equilibrations of solutions of $ThCl_4$ in the salt with the thorium-zinc alloy were carried out; x-ray diffraction patterns of the salt were obtained; and the absorption spectra of thorium chlorides dissolved in methyl alcohol were determined.

No reference to the Th-ThCl$_4$ phase diagram can be found in the literature. The study of this system was undertaken

to determine which chlorides exist and the phase equilibria
for these compounds as a function of temperature and composi-
tion. This information should lead to a better understanding
of the possible reactions of thorium in the LiCl-KCl eutectic,
liquid zinc system. Two possible equilibria involving
thorium in this system are

$$3ThCl_4(\text{in LiCl-KCl}) + \tfrac{1}{2}Th_2Zn_{17}(s) \rightleftharpoons 4ThCl_3(\text{in LiCl-KCl})$$
$$+ 8.5Zn(l) \qquad (5)$$

and

$$ThCl_4(\text{in LiCl-KCl}) + \tfrac{1}{2}Th_2Zn_{17}(s) \rightleftharpoons 2ThCl_2(\text{in LiCl-KCl})$$
$$+ 8.5Zn(l). \qquad (6)$$
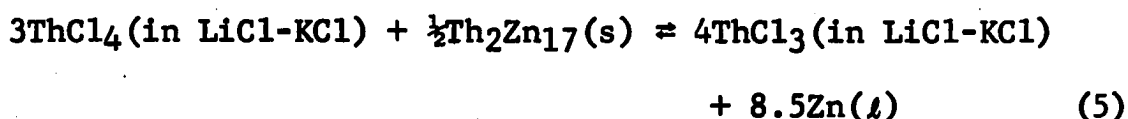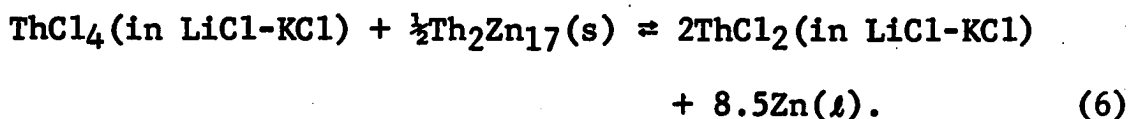
In a quantitative evaluation of the behavior of the thorium
chlorides in this system, a knowledge of the activity coeffi-
cients of the chlorides as well as their standard free
energies of formation and the standard free energy of forma-
tion of Th_2Zn_{17} is essential.

A great disparity exists in the literature among the
various values for the activity coefficient of thorium tetra-
chloride in the salt. Smirnov and Ivanovskii (8), who meas-
ured the e.m.f. of the cell $Th/ThCl_4,LiCl\text{-}KCl/Cl_2,C$, claimed
that solutions of up to 25 wt.% $ThCl_4$ in the salt (mole frac-
tion 4.75×10^{-2}) in the temperature range $480\text{-}893^{\circ}C$. behaved
ideally, i.e., the activity coefficient of $ThCl_4$ relative to

pure (liquid) $ThCl_4$ was unity. This would make their activity coefficient of the tetrachloride relative to pure solid $ThCl_4$ about 10 for these same composition ranges at 500°C. Inman, Bockris et al. (4) found, however, in their measurement of the e.m.f. of the cell $Th/ThCl_4$, LiCl-KCl/LiCl-KCl-AgCl/Ag, that the activity coefficient of $ThCl_4$ relative to pure solid $ThCl_4$ was about 1×10^{-5} at 420°C. for a mole fraction of $ThCl_4$ in the salt of 1.4×10^{-3}. Yang and Hudson (9) also made measurements of this cell but in the temperature range 500-550°C. They obtained values for γ_{ThCl_4} (activity coefficient) relative to pure solid $ThCl_4$ of about 1×10^{-3} for mole fraction values of 4.8×10^{-3} to 3.8×10^{-3} of $ThCl_4$ in the eutectic. In an attempt to determine the activity coefficient of $ThCl_4$ in the LiCl-KCl salt the e.m.f. of the cell $Th/ThCl_4$-LiCl-KCl//LiCl-KCl-3.3 wt.% AgCl/Ag was measured in the temperature range 450-650°C and at mole fraction values of $ThCl_4$ in the salt ranging from 1.53×10^{-4} to 6.65×10^{-2} (0.102 to 32.4 wt.% $ThCl_4$).

The pertinent free energy data used in this work are summarized in Table 1.

Table 1. Free energy data for thorium chlorides and Th_2Zn_{17},
$\Delta F^O = a + bT + cT \log T$ calories/mole

Compound	a	b	c	Temperature range, $^O K$
$ThCl_4$	-286,400	129.2	-19.3	298-1100
$ThCl_3$	-231,800	96.9	-13.8	"
$ThCl_2$	-172,900	62.9	-9.2	"
Th_2Zn_{17}	-145,000	72.1	--	723-1173

The standard free energy of formation of $ThCl_4$ was esti-
mated using Glassner's (10) ΔS^o_{298} and ΔH^o_{298}, -72.9 calories/
mole-degree and -284,500 calories/mole respectively, and a
mean ΔC_p for $ThCl_4$ of 8.4 calories/mole-degree for the temper-
ature range 298°-$1100^O K$. This ΔC_p was obtained by assuming
that each chlorine in the compound contributes 6.5 calories/
mole-degree to the heat capacity of the compound and that the
ΔC_p for the formation of the compound is due only to the dif-
ference between this value and the heat capacity of free
chlorine, 4.41 calories/degree-mole Cl (10). The values of
$\Delta F^o_{ThCl_4}$ at 500 and $700^O C$ agree well with the values obtained
from Glassner's much more complicated expression for ΔF^O and
also with those obtained by other investigators. The values
of $\Delta F^o_{ThCl_4}$ at 500 and $700^O C$ reported by various investigators

are listed in Table 2.

Table 2. Values of $\Delta F^O_{ThCl_4}$ in kilocalories/mole at 500 and 700°C

Reference	$\Delta F^O,500°C$	$\Delta F^O,700°C$
This work	-229.2	-216.7
Glassner (10)	-229.6	-216.3
Hamer (11)	-228.3	-214.3
Block and Wicks (12)	-227.7	-213.0
Smirnov (8)	-222.4	-207.9

$\Delta F^O_{ThCl_3}$ was estimated from Glassner's ΔH^O_{298}, -230 kilo-calories/mole (10), a mean ΔC_p of 6.0 calories/mole-degree, and -56.7 calories/mole-degree for ΔS^O_{298} of $ThCl_3$, a value slightly modified from Glassner's. The values of $\Delta F^O_{ThCl_3}$ obtained from this estimate at 500 and 700°C are -187.8 and -178.0 kilocalories/mole respectively; these again compare favorably with Glassner's (10) values of -188.2 and -178.3 kilocalories/mole obtained from a much more complicated expression for $\Delta F^O_{ThCl_3}$.

$\Delta F^O_{ThCl_2}$ was estimated using a mean ΔC_p of 4.0 calories/mole-degree and a ΔS^O_{298} of -36.1 calories/mole-degree which was estimated from the analogous value for $ZrCl_2$. The value for ΔH^O of $ThCl_2$ at 700°C was obtained in this work and will be discussed later. These results for $\Delta F^O_{ThCl_2}$ are in poor agreement with those of Smirnov (6) who reported to have

determined $\Delta F^O_{ThCl_2}$ from e.m.f. measurements of the cell

Th/LiCl-KCl-1.4 wt.% $ThCl_4$/Cl_2,C in which he assumed all of

the $ThCl_4$ was completely reduced with thorium to soluble

$ThCl_2$.

The equation for $\Delta F^O_{Th_2Zn_{17}}$ given in Table 1 represents

Chiotti and Gill's (13) values obtained from vapor pressure

measurements. These results agree poorly with those obtained

by Smirnov, Ivanovskii et al. (14). They use e.m.f. tech-

niques and found $\Delta F^O_{Th_2Zn_{17}}$ to be expressed as

$$\Delta F^O_{Th_2Zn_{17}} = -45,200 + 11.26T \text{ calories/mole,} \tag{7}$$

assuming a four electron process. However, their measurements

involved cells in which their thorium electrode was immersed

in pure $ThCl_4$ for long periods of time in the temperature

range 480-893°C. With the possibility of the $ThCl_4$ being

reduced by the thorium to lower chlorides in their cell, it

is not surprising that their results should differ from the

values obtained from vapor pressure measurements. The vapor

pressure measurements are probably the most accurate and will

be used in calculations in this work.

EXPERIMENTAL APPARATUS AND PROCEDURES

Experimental Apparatus

The experiments performed involving the thorium chlo-
rides and the thorium-zinc alloy can be divided roughly into
two types: batch-type experiments done with small quantities
of materials (about 50 grams total) and larger experiments
involving greater quantities (>500 grams) of these materials.

The smaller, batch-type experiments were done in tanta-
lum crucibles made from 20 mil, one inch O.D. tantalum tubing.
After a drawn tantalum cap was welded to one end of the
tubing, the charges were weighed and transferred to the cru-
cible. The crucible was then sealed by welding a tantalum
cap to the top. All these operations were performed in a dry
box under an atmosphere of argon. These crucibles were them-
selves sealed in stainless steel containers to prevent oxida-
tion and embrittlement of the tantalum at high temperatures.
The whole container was then placed in a temperature-
controlled resistance furnace which was rotated 180° at a
speed of about fifty oscillations per minute. This was done
to break any interfacial films and to promote the attainment
of chemical equilibrium. After the desired heating and set-
tling times were achieved, the assembly was water-quenched.

The charge was then cut open and the salt and metal phases sampled for subsequent chemical and metallographic analysis.

The larger experiments were done with large quantities of the salt and metal in a cell of the type shown in cross-section in Figure 1. The equipment used in association with this cell is shown in Figure 2. This equipment included (1) argon source, (2) argon purification train (calcium chips maintained at 630°C.), (3) mechanical vacuum pump, (4) mercury monometer, (5) temperature controller and indicator, (6) variable speed stirring motor, and (7) potentiometer.

The cell was constructed from Inconel-clad, 3½ inch I.D. mild steel pipe. The top of the pipe was flanged and fitted to a brass cover plate which was adapted with Cenco vacuum couplings for air-tight, electrically-insulated insertion of a reference electrode, thorium electrode, tantalum stirring paddle, tantalum thermocouple well, and two sight glasses.

The reference electrode used in these experiments was a silver-silver chloride electrode developed by Bockris et al. (15). The electrode was constructed from a 7 mm. pyrex tube with the bottom end blown into a very thin diaphragm. Into this tube was placed a few grams of KCl-LiCl eutectic containing 3.3 wt.% AgCl. A fifty mil silver wire was inserted

Figure 1. Cross-sectional diagram of cell

     1. Mild steel with stainless steel jacket
     2. Bakelite insulator
     3. Brass head
     4. Insulated bolts
     5. Cenco vacuum couplings
     6. "O" rings
     7. Cooling coils
     8. Tantalum crucible
     9. MgO insulator
   10. Thorium-saturated zinc phase
   11. Salt phase
   12. Tantalum stirring rod
   13. Tantalum thermocouple well
   14. Thorium electrode
   15. Silver-silver chloride reference electrode
   16. Sight glass
   17. To manometer
   18. To vacuum pump and argon source
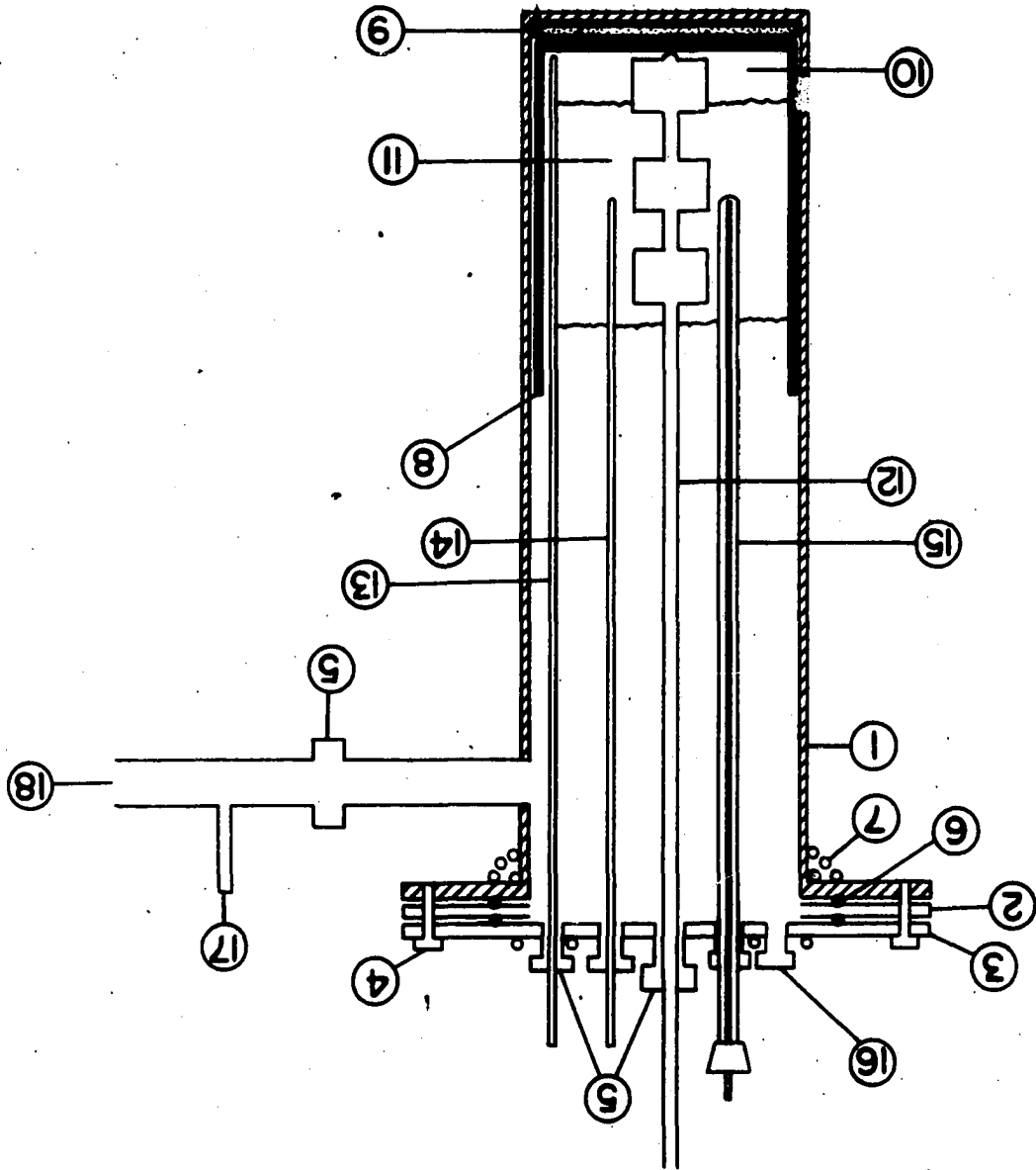
Figure 2. Schematic diagram of cell and associated equipment

1. Resistance furnace
2. Cell
3. External thermocouple for controller
4. Indicating controller
5. Mercury manometer
6. Mechanical pump
7. Toggle valves
8. Argon tank
9. Argon to sampling tubes
10. Argon purification train
11. Variable speed stirring motor
12. Leads to electrodes
13. Internal thermocouple
14. Ice bath
15. Potentiometer
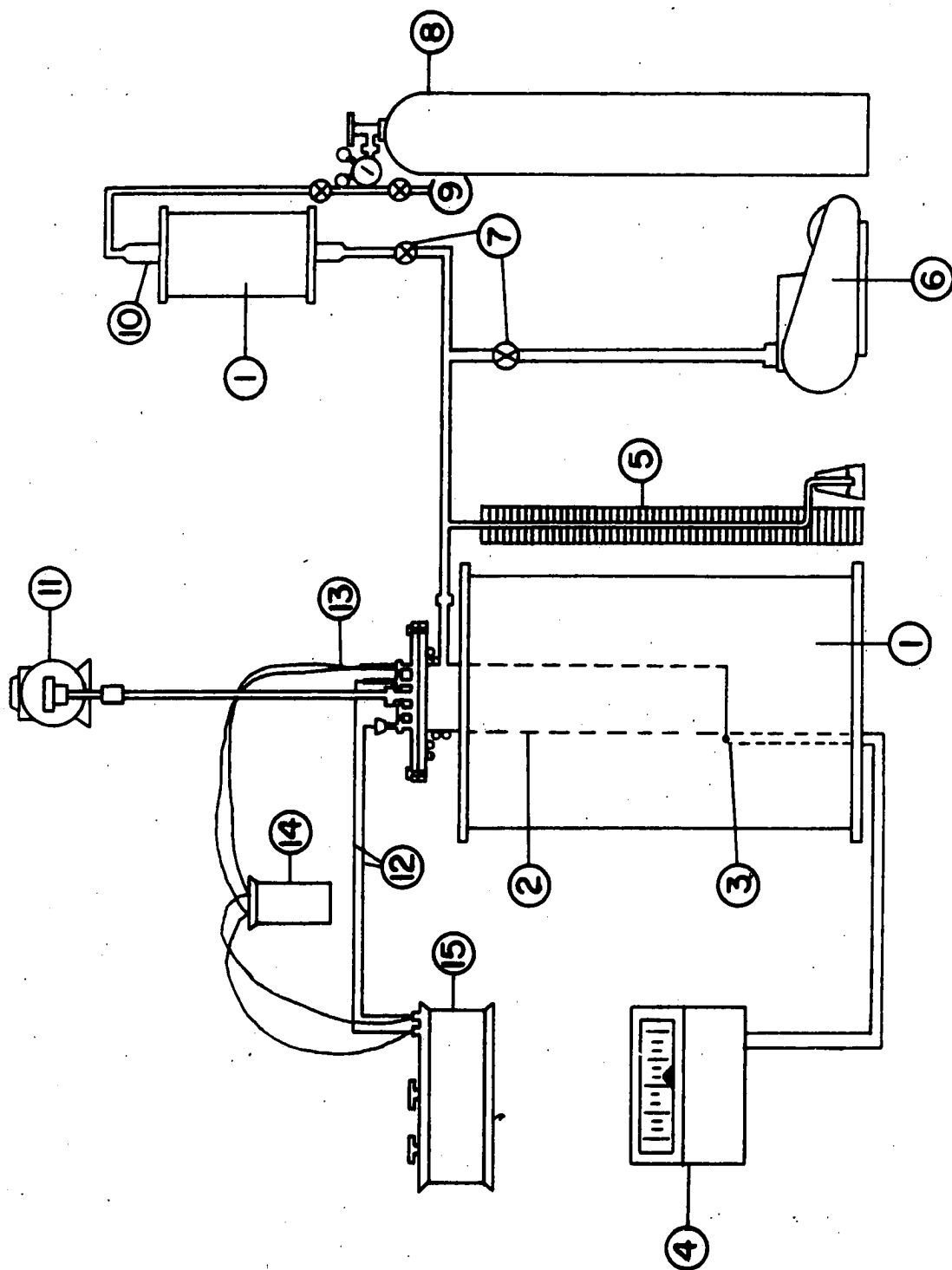
into this solution; the wire extended through a rubber stopper at the top end of the glass electrode. A small hole was made in the side of the pyrex tube of the reference electrode at a point inside the cell just below the brass head to maintain equal pressure on both sides of the thin glass diaphragm. Since the concentrations of the eutectic are essentially the same on either side of the thin glass membrane, the liquid junction potential at this membrane should be negligible.

The thorium electrode was constructed by swaging high purity, 1/8" thorium rod onto the end of a 1/8" tantalum rod using a 5/32" tantalum sheath. This method provided a firm joint with good metallic contact between the tantalum and thorium.

The stirring paddle was constructed from 1/4" tantalum rod onto which were welded small rectangular tantalum stirring fins. The tantalum rod extended up through a Cenco vacuum coupling to a variable speed stirring motor which was operated generally at a speed of 120 rpm.

The thermocouple well, constructed from 5/32" tantalum tubing sealed at one end, extended into the zinc phase and served as the electrode lead to the thorium-zinc alloy.

The tantalum crucible which contained the salt and metal

phases was separated from the bottom of the cell by an MgO

spacer. The tantalum crucible was 3 1/8" in outside diameter

and was rolled from 30 mil tantalum sheet. The crucible was

butt-welded along the vertical edge and closed at the bottom

with a spun tantalum cap which was heli-arc welded to the

cylinder.

The cell was heated with an eighteen ohm resistance fur-

nace, and the temperature was controlled to within $\pm$ 0.25^{o}C.

using a Bristol electronic indicating controller. The cell

was operated at slightly over one atmosphere of argon, which

had been passed for purification purposes over calcium chips

at 630°C., to avoid contamination from air and moisture.

The various e.m.f.'s as well as the thermocouple e.m.f.

were measured on a Rubicon B high precision potentiometer.

Experimental Procedures

Differential thermal analysis

Samples to be studied by differential thermal analysis

were first equilibrated in rocking-furnaces in tantalum

crucibles which had been fitted at the bottom with a thermo-

couple well. After the samples had been given the desired

heat treatment in the rocking furnace, thermocouples were

inserted into the sample thermocouple well and into a nickel

block adjacent to the sample. The whole assembly was then
placed in a resistance furnace. The temperature differential
between the sample and the nickel block was recorded as a
function of temperature both on heating and on cooling. The
heating and cooling rates used in these experiments were about
three to five degrees per minute.

Measurement of $ThCl_4$ activity

For the measurement of the activity of $ThCl_4$ in the LiCl-
KCl eutectic, the composition of the salt phase was varied by
making additions of $ThCl_4$ to the cell. The $ThCl_4$ was added
through a tantalum tube which was lowered into the cell
through one of the sight glass ports. The argon pressure in
the cell was increased enough so as to prevent the entrance
of any air into the cell but not so much as to blow the added
salt granules out of the cell. After the addition had been
made and the sight glass replaced, the mixture was stirred
for five or ten minutes.

Measurements of the e.m.f. developed between the thorium
electrode and the silver-silver chloride reference electrode
were made at the various salt compositions as a function of
temperature. The thorium electrode was removed between
measurements and cleaned by grinding with silicon carbide

paper and then etching with a solution of 1:1 HNO_3 containing a small amount of Na_2SiF_6. This procedure served to provide a new, fresh thorium surface for each measurement.

After the measurements were made, the salt was sampled by sucking up a few grams of the salt with a pipette bulb into an argon-filled pyrex tube which had been inserted into the cell through the sight glass port. These samples were then analyzed for their thorium content.

E.m.f. measurement of the cell $Th/LiCl-KCl,ThCl_x/Th_2Zn_{17}(s)$ in $Zn(\ell)$

In the measurement of the e.m.f. between the thorium electrode in the salt and the thorium-zinc alloy, any salt or alloy additions which were needed were added through the sight glass port in the same manner as above. After the desired e.m.f. measurements had been made, both the salt and metal phases were sampled. The salt samples were then analyzed for their thorium content and the metal samples were mounted, polished, and examined metallographically as a check on their composition.

X-ray diffraction

Samples to be x-rayed were crushed with a mortar and pestle in a dry box filled with argon and sealed in a 0.5 mm.

glass capillary. The capillary was then mounted in a Debye-Scherrer camera and exposed to nickel-filtered copper Kα radiation for twenty-four hours.

Absorption spectra

Absorption spectra of samples dissolved in methyl alcohol in 1 cm. quartz cells were determined at wavelengths of 450 to 220 millimicrons using a Model 14 Cary recording spectrophotometer.

Materials Preparation

LiCl-55.6 wt.% KCl eutectic solvent

The method employed in the preparation of this solvent was essentially that used successfully by Laitinen and others (16, 17). Analytical Reagent grade KCl and LiCl were mixed in the proper proportions in a pyrex tube. The salt was then heated under vacuum for four hours to remove moisture. After this, HCl gas was continuously passed through the salt while it was still solid, as it was melting, and after it was liquid. Purified argon gas was then flushed through the system to remove any residual HCl, and the molten salt was then pumped on again. After this treatment, the molten salt was siphoned through a sintered glass filter to remove any

foreign matter and collected in a cleaned tantalum crucible

housed in a bell jar. The salt was then allowed to cool

under vacuum to be ready for use when needed. A diagram of

the apparatus used in the preparation of the LiCl-KCl solvent

is shown in Figure 3. The design and construction of this

apparatus was a joint effort of W. C. Robinson, Jr., J. S.

Klepfer, and the author.

AgCl-LiCl-KCl for silver-silver chloride reference electrode

The first step in the preparation of this salt mixture

was the preparation of good, dry silver chloride. $AgNO_3$ was

added to a solution of 0.1M HCl to precipitate AgCl. This

was done in a darkroom to prevent photochemical decomposition

of the silver chloride by light. The silver chloride was

then dried at 105°C. to constant weight and dissolved in LiCl-

KCl eutectic. The mixture was heated to 525°C., stirred, and

siphoned into 4 mm. I.D. pyrex tubes. The resulting cylinders

did not wet the pyrex and were easily removed from the tubes

in a dry box and stored in the dark in a desicator until

needed for use in a reference electrode. The resulting cylin-

ders of AgCl-LiCl-KCl fit nicely into the 7 mm. tubing used

for the reference electrode, thus facilitating preparation of

the reference electrodes. The salt was analyzed for silver

Figure 3. Diagram of apparatus for preparation of LiCl-KCl eutectic

ARGON
PURIFICATION
TRAIN

DISCHARGE TO HOOD
THROUGH ACID NEUTRALIZER

ANHYDROUS
HCl TANK

COLD TRAP

HCl INLET HOOK-UP

ARGON
TANK

SALT OUTLET
HOOK-UP

MERCURY
MANOMETER

SALT
DISCHARGE
HOUSING

RESISTANCE
FURNACE

INDICATING
CONTROLLER

VACUUM PUMP

THERMOCOUPLE
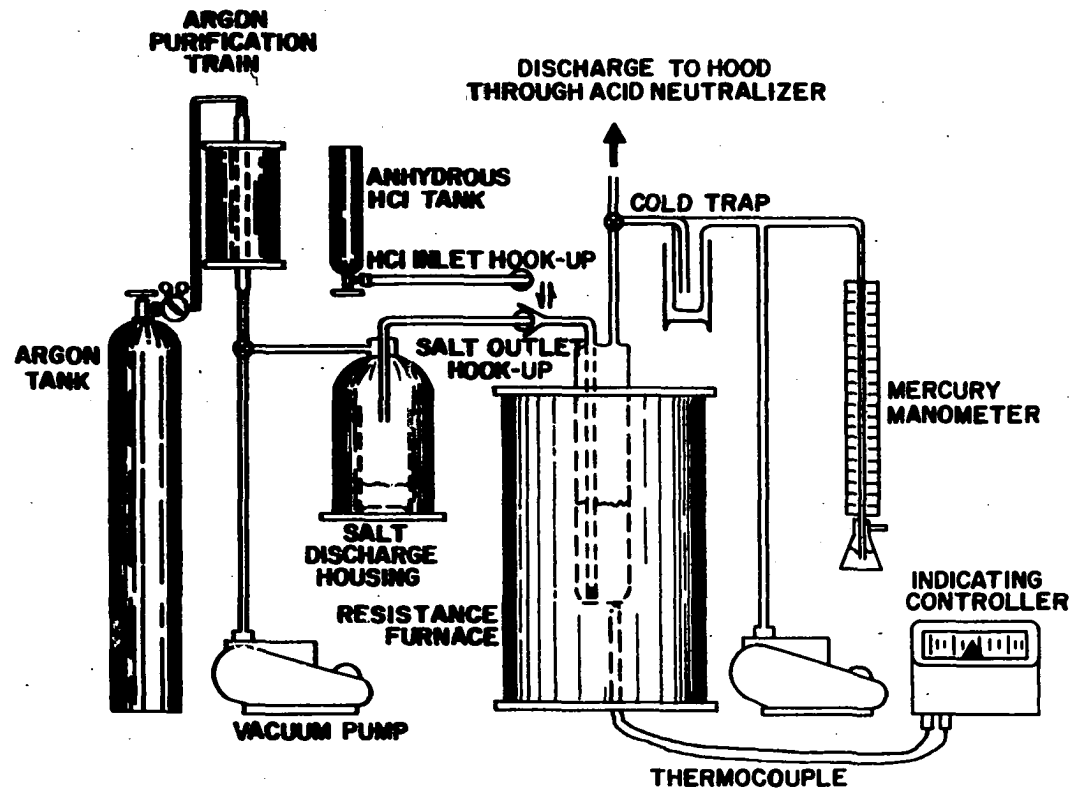
chloride and found to contain 3.33 wt.% AgCl (N_{AgCl} = 1.319 x 10^{-2}). This concentration of silver chloride in the salt was used for all reference electrodes used.

$ThCl_4$

The thorium tetrachloride used in these experiments was prepared by Krupp, Schmidt, and Peterson in their development of a process for the production of high purity thorium (18).

The first step in the process is the conversion of the hydrated thorium oxalate to thorium dioxide by heating at 300°C. for seven days. The thorium dioxide is then mixed with carbon and exposed to chlorine gas at 600°C. to form crude $ThCl_4$. This crude product is sublimed three times onto a water-cooled, cold finger condenser, the second and third sublimations being done over thorium chips at 750°C. to remove the small amounts of iron, manganese, and chromium chlorides which otherwise would sublime with the thorium tetrachloride. The purified $ThCl_4$ is then collected and stored in an inert atmosphere until needed.

Zinc-10 wt.% thorium alloy

The thorium-zinc alloy was prepared by sealing cleaned thorium and zinc in the proper proportions in a tantalum crucible under an argon atmosphere. The crucible was then

itself sealed in a stainless steel crucible, equilibrated slightly above the melting point of the alloy (900°C.) in an oscillating furnace for eight to sixteen hours, and water-quenched. The tantalum was then peeled from the alloy and the outer skin lathed off to remove the tantalum-thorium-oxygen mixture present on the surface of the alloy. The alloy was then kept under argon until needed.

Chemical Analysis of Salt Phase for Thorium

For salts containing less than one weight per cent thorium, a spectrophotometric procedure was used (19). The complexing reagent used is commonly known as Thorin (2-(2-hydroxy-3,6,-disulfo-1-naphthylazo)benzenearsonic acid). The determinations were done at a wavelength of 545 millimicrons.

For salts containing more than one weight per cent thorium, an E.D.T.A. (Ethylenediaminetetracetic acid) titration using Xylenol Orange indicator (20) was used. The pH was kept between 2.5 and 3.5, and the titration was done to a red-to-yellow color change end point.

EXPERIMENTAL RESULTS AND DISCUSSION

Investigation of the Th-ThCl₄ Phase Diagram

Differential thermal analyses (D.T.A) were done on pre-equilibrated mixtures of thorium and thorium tetrachloride to determine the Th-ThCl₄ phase diagram. The thermal arrests found for the various composition mixtures are listed in Table 3.

Table 3. Composition and thermal arrests of pre-equilibrated Th-ThCl₄ mixtures

Grams Th	Grams ThCl₄	N_{Th}	Thermal arrests	Pre-equilibration history			
				$T^{o}C$	days	$T^{o}C$	days
0.47	10.02	.065	709,743	830	3	555	4
0.76	10.03	.114	712,739	775	1	520	1
1.42	9.95	.190	708,737	775	1	520	1
2.02	9.89	.242	710,714	840	2	530	1½
2.85	9.92	.314	710,738	840	2	530	1½
3.60	9.84	.367	710,744,753	835	3	550	4
4.65	9.84	.431	709,748	835	3	550	4
6.08	10.12	.490	709,745	830	3	555	4
1.95	10.21	.218	697,708,725	810	1½	515	1
2.11	10.17	.250	700,711	800	1	500	1
1.28	6.12	.292	697,710,727	800	1	500	1
3.28	9.76	.351	700,711,743	810	1½	515	1

The phase diagram indicated by these data is shown in Figure 4.

The freezing point of ThCl₄ was found on cooling to be 746°C. The accepted literature value (12) for the melting

Figure 4. Tentative Th-ThCl4 phase diagram indicated by
          differential thermal analysis
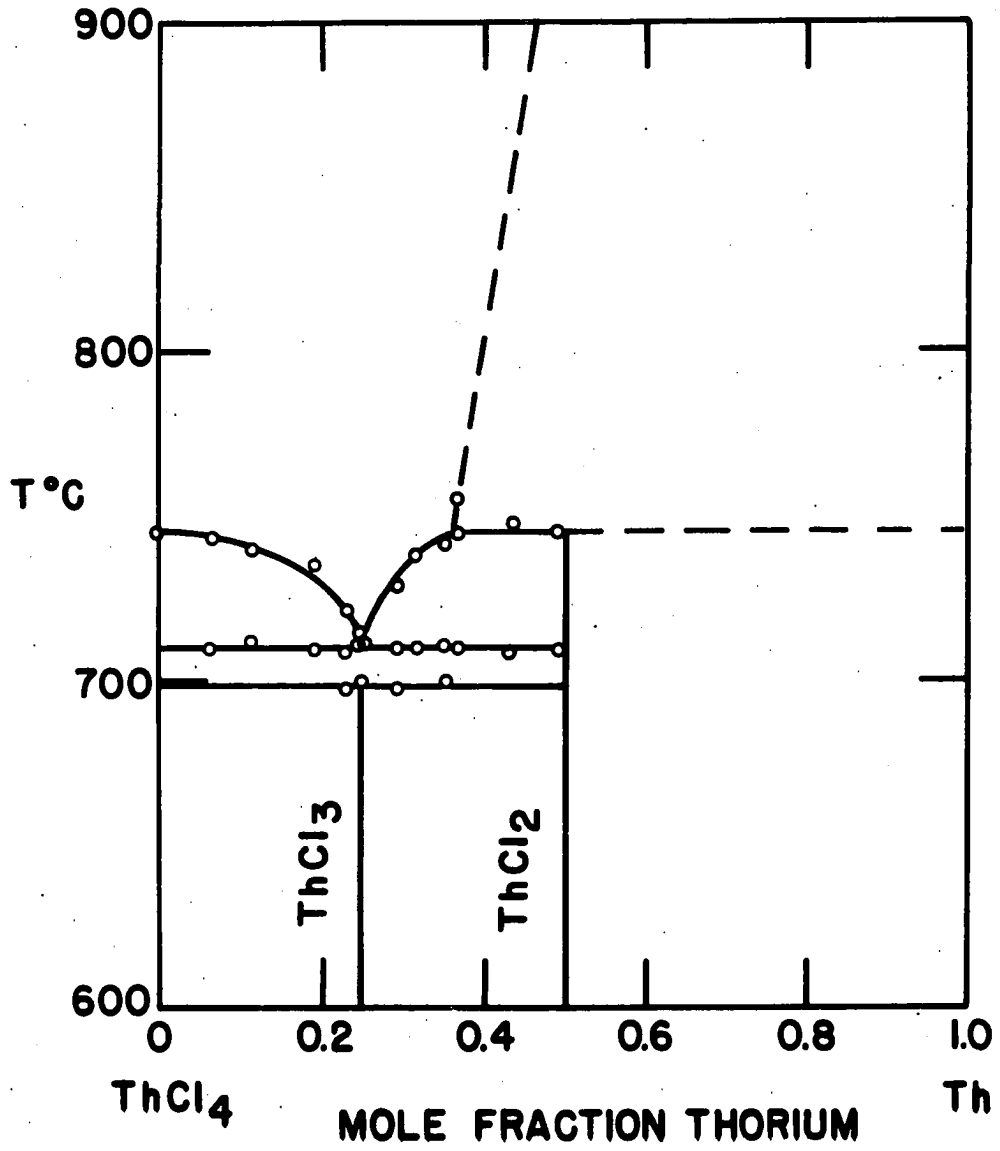
point of $ThCl_4$ is about 765°C; therefore it is possible that the upper thermal arrests on the phase diagram are somewhat low. The arrests at 710°C, however, were extremely strong and should be accurate within one or two degrees. The thermal arrests found at 698°C were not observed on cooling but only on heating after the samples had been held at about 665°C for several hours. These observations suggested that $ThCl_3$, as indicated by the phase diagram, is produced by a peritectoid reaction on cooling. Since solid-state diffusion processes are slow, the formation of $ThCl_3$ should require an appreciable period of time. The arrests obtained on heating were small and showed only a small amount of heat being absorbed.

These data indicate that on heating to 698°C, $ThCl_3$ disproportionates to $ThCl_2$ and $ThCl_4$, the equilibrium being

$$2ThCl_3 \rightleftarrows ThCl_4 + ThCl_2. \tag{8}$$
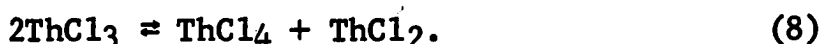
If there is little or no mutual solubility, as indicated in the phase diagram, all products and reactants are in their standard states, then $\Delta F°$ for this reaction is zero at 698°C. Therefore at this temperature,

$$\Delta F°_{ThCl_4} + \Delta F°_{ThCl_2} = 2\Delta F°_{ThCl_3}. \tag{9}$$

From the values for $\Delta F°_{ThCl_4}$ and $\Delta F°_{ThCl_3}$ at 698°C given in Table 1, one obtains a value of -139.3 kilocalories/mole for

$\Delta F^{O}_{ThCl_2}$ at 698°C. The values of ΔS^{O}_{298} and ΔC_p for $ThCl_2$ discussed in the Introduction give the following equation for $\Delta S^{O}_{ThCl_2}$:

$$\Delta S^{O}_{ThCl_2} = -58.9 + 9.2 \log T \text{ calories/mole-degree.} \quad (10)$$

This equation gives a value of -31.4 calories/mole-degree for $\Delta S^{O}_{ThCl_2}$ at 698°C. Since $\Delta F^{O}_{ThCl_2}$ is equal to $\Delta H^{O}_{ThCl_2} - T\Delta S^{O}_{ThCl_2}$, $\Delta H^{O}_{ThCl_2}$ at 698°C (971°K) is calculated to be -170.3 kilocalories/mole. Therefore the general equation for $\Delta H^{O}_{ThCl_2}$ may be written

$$\Delta H^{O}_{ThCl_2,T} = \Delta H^{O}_{ThCl_2,971} + \int_{971}^{T} \Delta C_p dT$$

$$= -172,900 + 4.0T \text{ calories/mole.} \quad (11)$$

Equations 10 and 11 combine to give the following equation for $\Delta F^{O}_{ThCl_2}$:

$$\Delta F^{O}_{ThCl_2} = -172,900 + 62.9T - 9.2T \log T \text{ calories/mole.} \quad (12)$$

This is the equation given for $\Delta F^{O}_{ThCl_2}$ in the Introduction.

To verify that $ThCl_3$ can be formed by equilibrating $ThCl_4$ and thorium in the proper proportions at temperatures below 698°C., a charge consisting of 4.10 grams of thorium and 18.59 grams of $ThCl_4$ was equilibrated at 800°C for twenty-six hours, water-quenched, and then equilibrated at 650°C for sixty-four hours. The resulting product was purplish-black in color with

very little remaining thorium evident. The product was heated under vacuum at 500°C for two hours to remove any unreacted $ThCl_4$. The residue analyzed 33.2 wt.% Cl and 66.3 wt.% Th, giving a chlorine to thorium ratio of 3.2 to 1. An x-ray powder pattern of this material showed some weak $ThCl_4$ lines plus many other lines assumed to be those of $ThCl_3$. No lines which might be attributed to thorium were found. The measured 2θ values and the calculated d spacings of these lines as well as those of $ThCl_4$ are given in Table 4. The $ThCl_3$ lines could not be indexed and probably represent a unit cell of orthorhombic or lower symmetry.

The phase diagram shown in Figure 4 indicates that $ThCl_2$ decomposes peritectically at about 748°C. In an attempt to prepare this compound, a charge of 5.34 grams of thorium and 9.70 grams of $ThCl_4$ was equilibrated for twenty-six hours at 800°C., water-quenched, and then equilibrated at 715°C for sixty-four hours. After equilibration 3.91 grams of thorium still remained. The fact that thorium remained in the preparation of $ThCl_2$ indicates that this reaction is slow and that the reaction had not proceeded to completion. A dark, gray-black material was found on the surface of the thorium metal. This material was analyzed for thorium and chlorine. The

resulting analyses were 76.3 wt.% Th and 24.0 wt.% Cl compared with theoretical percentages of 76.6 wt.% Th and 23.4 wt.% Cl for $ThCl_2$. The chemical analyses obtained give a chlorine to thorium ratio for the material of 2.02 to 1. An x-ray powder pattern was taken of this material which is believed to be $ThCl_2$. The measured 2θ values and the calculated d spacings are listed in Table 4. These lines could not be indexed and probably represent a unit cell of orthorhombic or lower symmetry. It should be noted here that both of these products, believed to be $ThCl_3$ and $ThCl_2$, formed from the reduction of $ThCl_4$ with thorium, are very hygroscopic and necessarily were handled in a dry-box under an atmosphere of argon.

Table 4. Measured 2θ values and calculated d spacings of the thorium chlorides (S = strong, M = medium, W = weak)

	$ThCl_4$			$ThCl_3$			$ThCl_2$	
RI*	2θ	d	RI	2θ	d	RI	2θ	d
S	15.568	5.687	M	11.643	7.593	M	13.565	6.520
VS	15.885	5.574	W	12.636	6.999	VS	15.616	5.670
S	20.977	4.231	W	14.645	6.043	W	16.710	5.301
S	24.031	3.700	M	15.309	5.782	S	17.750	4.992
W	24.927	3.569	S	16.921	5.235	M	20.720	4.283
S	26.315	3.384	W	18.798	4.716	S	22.246	3.993
S	28.140	3.168	M	19.360	4.581	W	26.531	3.357
S	31.956	2.798	S	25.276	3.520	S	27.165	3.280
S	33.847	2.646	S	27.305	3.263	M	28.505	3.129
VS	37.532	2.394	W	28.777	3.099	W	33.223	2.694

*RI = relative intensity.

Table 4. (Continued)

ThCl4			ThCl3			ThCl2		
RI	2θ	d	RI	2θ	d	RI	2θ	d
W	39.520	2.278	M	29.572	3.018	M	36.335	2.470
S	40.061	2.249	VW	30.222	2.954	M	38.680	2.326
S	41.348	2.182	S	31.050	2.877	S	40.255	2.238
M	42.524	2.124	VW	32.126	2.784	S	41.795	2.160
M	43.341	2.086	VW	33.056	2.707	W	44.661	2.027
M	45.588	1.988	VW	33.406	2.680	W	45.193	2.004
W	46.610	1.947	S	34.212	2.619	W	46.369	1.957
W	47.384	1.917	M	35.520	2.525	W	48.094	1.890
M	51.793	1.764	W	36.404	2.466	W	48.858	1.862
M	53.446	1.713	W	37.076	2.422	VW	49.858	1.827
M	55.374	1.658	S	38.966	2.309	VW	51.858	1.762
M	57.970	1.589	M	40.206	2.241	M	53.305	1.717
W	60.891	1.520	W	40.485	2.226	W	55.369	1.658
W	62.787	1.478	M	42.017	2.148	W	56.269	1.633
W	63.421	1.465	S	44.935	2.015	W	57.269	1.607
W	64.504	1.443	S	46.690	1.944	W	58.685	1.568
W	64.936	1.435	W	47.080	1.929	W	62.113	1.493
M	66.436	1.406	VW	48.952	1.859	W	65.393	1.426
M	67.103	1.394	W	52.624	1.738	W	67.785	1.394
VW	68.288	1.372	VW	54.803	1.674	W	69.537	1.351
W	69.124	1.358	W	56.111	1.636	W	71.123	1.324
M	70.489	1.334	W	57.324	1.606	W	72.257	1.306
M	75.024	1.265	W	59.176	1.560	VW	73.765	1.283
M	78.000	1.224	W	60.395	1.531	VW	76.416	1.245
M	84.431	1.146	W	61.294	1.511	VW	77.416	1.232
W	85.695	1.133	M	62.076	1.494			
W	85.765	1.132	W	69.596	1.350			
W	89.545	1.094	W	72.556	1.302			
W	90.375	1.086	W	73.924	1.281			
W	91.986	1.071						
W	96.610	1.032						
W	100.731	1.000						

Two other types of experiments were tried in attempts to prepare ThCl$_2$. It was anticipated that ThCl$_2$ would be insoluble in LiCl-KCl eutectic since ZrCl$_2$ has been found to be

very insoluble in this salt (4,21,22) and thorium often

behaves very much like zirconium in its chemistry. The first

experiment involved addition of 15.4 grams of a Zn-45.3 wt.%

Mg alloy to a system in which a solution of $ThCl_4$ in LiCl-KCl

eutectic was in contact with a Zn-8.1 wt.% Th alloy. The

system contained a solution of 131.4 grams of $ThCl_4$ in 350

grams of LiCl-KCl in contact with 241 grams of the Zn-8.1 wt.%

Th alloy. The charge was stirred for three hours at 500°C and

allowed to settle for one hour. The salt was then sampled and

analyzed for thorium and magnesium. The resulting analyses

were 2.95 wt.% Th and 1.86 wt.% Mg. The possible reactions

which might occur under these conditions are

$$ThCl_4 + 8.5Zn + 2Mg \rightarrow \tfrac{1}{2}Th_2Zn_{17} + 2MgCl_2 \qquad (13)$$

$$ThCl_4 + \tfrac{1}{2}Mg \rightarrow ThCl_3 + \tfrac{1}{2}MgCl_2 \qquad (14a)$$

and $$ThCl_4 + Mg \rightarrow MgCl_2 + ThCl_2 \downarrow \qquad (14b)$$
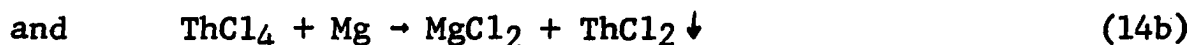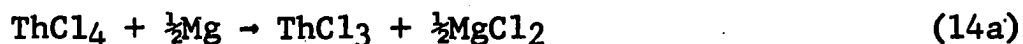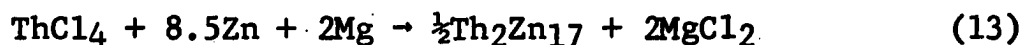
If Reaction 13 were the only reaction that occurred, the final

salt analysis should have been 10.6 wt.% Th and 1.54 wt.% Mg;

if only Reaction 14a occurred to form soluble $ThCl_3$, the

thorium content of the salt should have remained unchanged at

about 17 wt.% Th; if only Reaction 14b occurred, the final

salt analysis should have been 3.72 wt.% Th and 1.75 wt.% Mg.

The actual analyses of 2.95 wt.% Th and 1.86 wt.% Mg found in

the salt indicate that a reaction such as Reaction 14b
occurred.

A gray-black precipitate was found at the salt-metal
interface. Since a fair amount of LiCl and KCl would be
expected to be present with the precipitate from the LiCl-KCl
solution, a direct chlorine and thorium analysis to give the
amount of chlorine associated with the thorium in the material
could not be made. However, KCl is essentially insoluble in
methyl alcohol whereas LiCl is soluble in this solvent (23).
The gray precipitate was also found to be soluble to an apprec-
iable extent in the methyl alcohol. The presence of thorium
was shown by the appearance of a red-orange color in the alco-
hol when Thorin, a material which forms a red-orange complex
with thorium (19), was added to the alcohol solution. A solu-
tion of methyl alcohol into which the gray precipitate had
been extracted was analyzed for lithium, chlorine, and throium.
The chemical analysis of the alcohol solution was found to be
1.28 mg. Li/ml., 8.35 mg. Cl/ml., and 5.85 mg. Th/ml. A one-
to-one atom correspondence between lithium and chlorine was
assumed and the remaining chlorine gave a Cl/Th ratio of 2.02
to 1, indicating that the precipitate might be $ThCl_2$. (This
method of analysis was checked with $ThCl_4$ in methyl alcohol

and found to be valid). However, an x-ray powder pattern taken of the precipitate showed, in addition to LiCl and KCl lines, a group of lines which do not match those attributed to $ThCl_2$ in Table 4. The measured 2θ values and the calculated d spacings for the diffraction lines of this precipitate are given in Table 6. These data could be explained if a salt of the type $ThCl_2 \cdot xLiCl \cdot yKCl$ were being precipitated from the LiCl-KCl solution. The other possibility, that this precipitate is $ThOCl_2$, was considered, but, as will be discussed later, was shown not to be the case.

In the second type of experiment designed to precipitate $ThCl_2$ from the LiCl-KCl eutectic, calcium metal was equilibrated with solutions of $ThCl_4$ in the LiCl-KCl eutectic at $500^\circ C$. The details of the two such experiments done are given in Table 5.

Table 5. Data for the reduction of $ThCl_4$ in LiCl-KCl with calcium at $500^\circ C$

Experiment	Initial charge (gms.)			Thermal history	Final salt analysis, wt.% Th
	LiCl-KCl	$ThCl_4$	Ca		
4-5-1	22.378	17.438	1.898	Rocking-26 hrs. Settling-½ hr.	14.9
4-8-2	19.963	2.539	0.270	Rocking-28 hrs. Settling-3/4 hr.	3.65

Again there are three possible reactions which might occur:

$$ThCl_4 + \tfrac{1}{2}Ca \rightarrow ThCl_3 + \tfrac{1}{2}CaCl_2 \qquad (15a)$$

$$ThCl_4 + Ca \rightarrow CaCl_2 + ThCl_2\!\downarrow \qquad (15b)$$

and $\qquad ThCl_4 + 2Ca \rightarrow Th + 2CaCl_2. \qquad\qquad (16)$
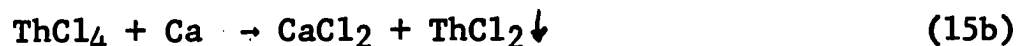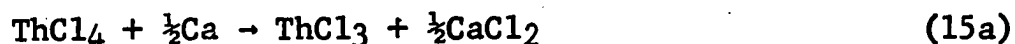
If Reaction 15a were the only reaction that occurred, the thorium content of the salt should have remained at the initial levels of 27.2 and 7.0 wt.% Th for the two experiments. If Reaction 15b were the only reaction that occurred, the weights used in these experiments were such that the salts should have been essentially stripped of thorium. If Reaction 16 were the only reaction that occurred, the final salt analyses should have been 14.9 and 3.6 wt.% Th respectively for the two experiments. These latter figures agree well with those actually found. This would indicate that in this system, Reaction 16 occurred. An x-ray diffraction pattern taken of a dark material found in experiment 4-5-1 showed, however, in addition to thorium lines, a group of lines which match very closely the pattern obtained from the precipitate formed from the reduction of the $ThCl_4$ with the zinc-magnesium alloy. The measured 2θ values and the calculated d spacings of this pattern are given in Table 6 along with the d spacings of LiCl, KCl, and Th as listed in the A.S.T.M. file.

Table 6. Measured 2θ values and calculated d spacings of the precipitates formed from reduction of ThCl₄ in LiCl-KCl with Zn-45.3 wt.% Mg and with Ca (S = strong, M = medium, W = weak, RI = relative intensity)

ThCl₄(in LiCl-KCl) + Zn-Mg product			ThCl₄(in LiCl-KCl) + Ca product			LiCl	KCl	Th
RI	2θ	d	RI	2θ	d	d	d	d
S	14.077	6.286	VS	13.956	6.340	2.967	3.146	2.93
S	16.317	5.428	S	16.198	5.467	2.570	2.224	2.54
S	23.234	3.825	S	22.986	3.866	1.817	1.816	1.79
S	27.279	3.296	VW	24.128	3.686	1.550	1.573	1.52
S	28.557	3.123	M	27.088	3.289	1.484	1.407	1.463
VS	30.185	2.958	VS	28.378	3.142	1.285	1.284	1.268
S	31.752	2.816	VS	30.346	2.943	1.179	1.113	1.162
S	32.942	2.717	VW	32.829	2.726	1.149	1.049	1.135
VS	35.013	2.561	VW	34.418	2.603	1.049		1.035
S	36.039	2.490	S	34.985	2.562			0.977
W	36.927	2.432	VW	36.859	2.436			0.897
VS	40.648	2.218	S	40.528	2.224			
S	43.115	2.096	W	42.957	2.104			
VW	45.881	1.976	VW	45.943	1.973			
VW	47.179	1.925	VW	47.125	1.927			
VW	49.413	1.843	VW	49.398	1.843			
VS	50.246	1.814	S	50.228	1.815			
VW	52.575	1.739	M	50.906	1.792			
VW	54.299	1.688	VW	54.418	1.684			
VW	57.905	1.591	VW	58.653	1.572			
VW	58.793	1.569	M	59.616	1.549			
VS	59.654	1.549	S	60.435	1.530			
VS	62.559	1.484	M	62.651	1.481			
W	63.858	1.456	M	63.470	1.464			
VS	66.541	1.404	W	66.533	1.404			
VS	73.873	1.282	M	73.731	1.284			
VS	81.657	1.178	W	81.623	1.178			
VS	84.236	1.148	W	82.747	1.165			
			W	84.166	1.149			
			W	85.387	1.136			

These data indicate that after Reaction 16 had occurred to give thorium metal, a reaction between this metal and the remaining $ThCl_4$ occurred to form a film on the surface of the thorium. This material and the precipitate formed from the reduction of $ThCl_4$ in LiCl-KCl with the zinc-magnesium alloy are evidently the same.

An effort was made to prepare $ThOCl_2$ to check that none of the groups of x-ray diffraction lines listed in Tables 4 and 6 are those of $ThOCl_2$. A charge of 19.77 grams of $ThCl_4$ and 13.99 grams of ThO_2 was heated at $800^{\circ}C$ for fifty-five hours and then water-quenched. The reaction here should be

$$ThCl_4 + ThO_2 \rightarrow 2ThOCl_2. \tag{17}$$
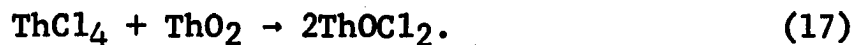
The resulting product was composed of white, fluffy, acicular crystals. Wylie et al. (24) found similar characteristics for $ThOI_2$. They reported that their $ThOI_2$ was "a felted mass of colorless, highly acicular crystals". This description aptly described the $ThOCl_2$ formed in this experiment. The $ThOCl_2$ analyzed 72.3 wt.% Th and 22.0 wt.% chlorine which compare well with the theoretical percentages: 72.7 wt.% Th and 22.2 wt.% Cl. An x-ray powder pattern was taken of the $ThOCl_2$. The measured 2θ values and the calculated d spacings are given in Table 7. From the large number of lines it would

Table 7. Measured 2θ and calculated d spacings for ThOCl₂
(S = strong, M = medium, W = Weak, RI = relative
intensity

RI	2θ	d	RI	2θ	d	RI	2θ	d
M	9.734*	9.083	VW	37.845*	2.376	S	59.875	1.543
VS	11.327*	7.808	VW	39.149	2.299	M	60.772	1.523
W	12.592	7.024	S	40.301*	2.235	W	61.578	1.505
W	13.265	6.669	M	41.282	2.185	W	61.940	1.497
VW	15.017*	5.894	M	41.808	2.159	M	62.922	1.476
M	15.748*	5.623	M	42.222	2.138	M	64.501	1.443
M	18.607*	4.764	M	44.032*	2.055	M	66.685	1.401
M	19.610*	4.524	W	45.842	1.978	W	67.449	1.387
VS	22.670*	3.919	M	46.912	1.935	VW	68.580	1.367
S	25.005*	3.558	M	48.404	1.879	M	70.117	1.341
VW	26.361	3.378	M	48.807	1.864	M	71.051	1.326
S	27.097*	3.276	M	49.498	1.841	VW	72.485	1.303
W	29.463	3.029	M	50.124	1.818	VW	72.815	1.298
M	30.361	2.941	M	50.599	1.802	W	73.628	1.286
M	31.805	2.811	M	51.443	1.775	M	74.353	1.275
M	32.646	2.740	M	52.027	1.756	VW	75.248	1.262
S	33.864*	2.644	VW	52.679	1.736	M	76.482	1.244
M	34.649	2.586	S	53.790	1.703	VW	77.365	1.232
M	34.877	2.570	M	54.751	1.675	VW	78.762	1.214
S	35.317	2.539	M	56.173	1.636	M	80.101	1.197
S	36.390	2.467	VW	57.235	1.608	VW	81.977	1.174
S	36.887	2.435	VW	59.113	1.561	VW	82.532	1.168
VW	83.930	1.152	W	91.107	1.079	VW	100.343	1.003
W	85.227	1.138	W	92.564	1.066	VW	101.867	0.992
VW	86.283	1.126	M	93.521	1.057	M	103.900*	0.978
VW	88.037	1.108	M	97.624*	1.024	M	105.704*	0.966
W	90.283	1.087	M	98.664*	1.016	W	108.212	0.951

*Represents average of split line.

appear that either the unit cell is very large or is of very low symmetry. Some of the higher d spacing lines listed in Table 7 are averages of diffraction lines which showed splitting, probably due to an absorption effect.

Absorption spectra in methyl alcohol of $ThCl_4$, and the prepared $ThCl_3$, $ThCl_2$, and $ThOCl_2$ as well as those of the precipitates formed by reduction of $ThCl_4$ in LiCl-KCl with zinc-magnesium and with calcium were determined and are shown in Figure 5. This was done mostly as a qualitative check on the similarity or dissimilarity of these materials and not as an effort to determine absorption coefficients. Thorium tetrachloride shows small peaks at 356, 324, 270, and 254 millimicrons (mμ) and a large peak at 226 mμ. The $ThOCl_2$ on the other hand shows no maxima in the wavelength span investigated. The $ThCl_3$ prepared from the reduction of $ThCl_4$ with thorium metal shows small peaks at 361 and 290 mμ and apparently a much larger peak somewhere below 220 mμ. The $ThCl_2$ prepared from the reduction of $ThCl_4$ with thorium shows peaks at 361 and 317 mμ with a somewhat larger one at 241 mμ. It is interesting to note that the precipitates formed from the reduction of $ThCl_4$ in LiCl-KCl with Zn-45.3 wt.% Mg and with calcium give spectra similar to that of the $ThCl_2$ prepared by

Figure 5. Absorption spectra of thorium chlorides in methyl alcohol
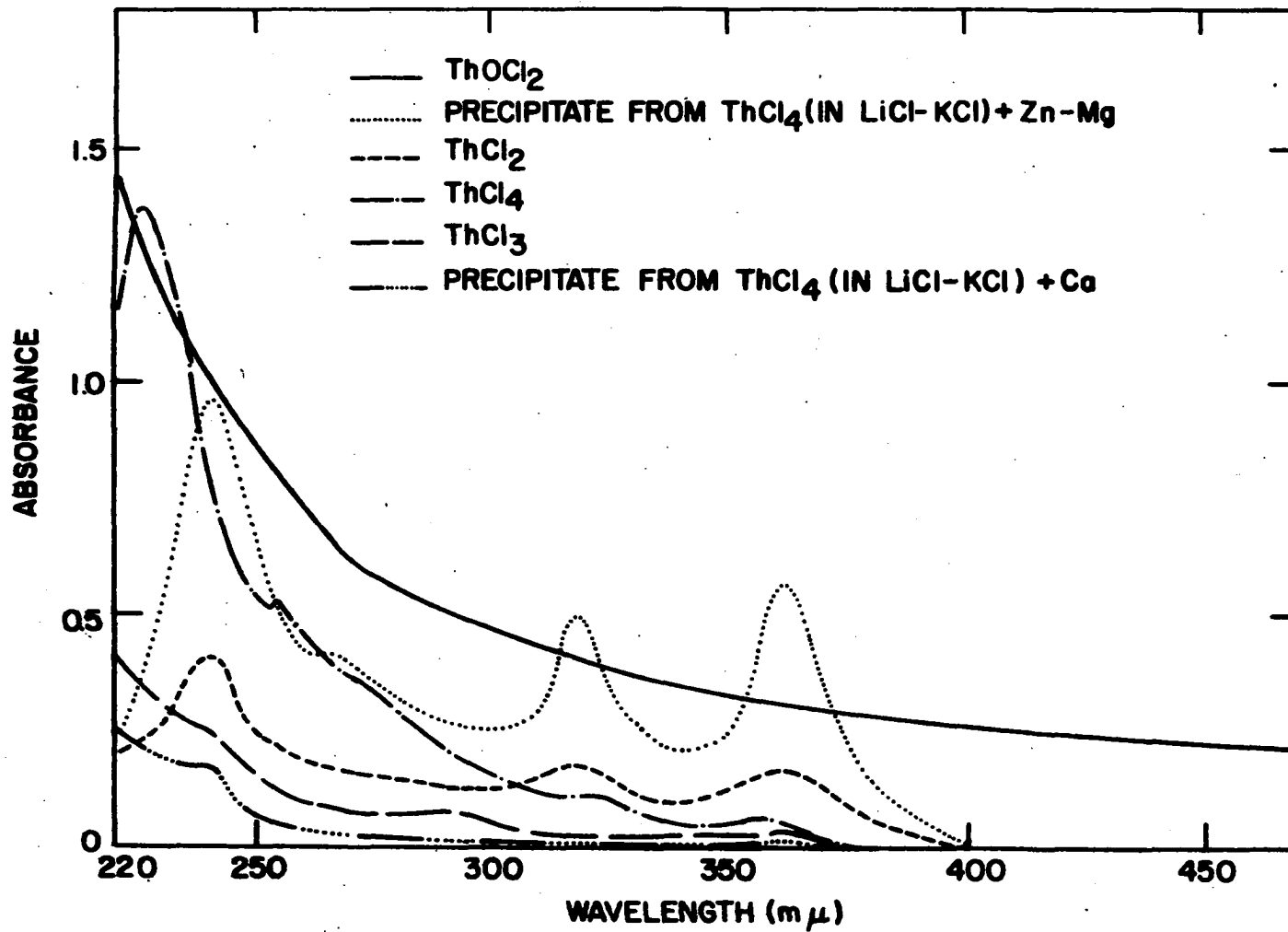
reaction of thorium and ThCl$_4$ even though the x-ray patterns were different. This would indicate that the alcoholated species in solution are the same for all three cases. The fact that the precipitates and the ThCl$_2$ give the same absorption spectra but different x-ray patterns suggests that the precipitate is some salt of the type ThCl$_2$·xLiCl·yKCl. The x-ray diffraction patterns of this salt and of ThCl$_2$ would be expected to be different, but their absorption spectra in methyl alcohol could be the same.

Activity Coefficients of Thorium Chlorides
in LiCl-KCl Eutectic

As was mentioned in the Introduction, in order to make calculations as to the extent of Reactions 5 and 6, the activity coefficients of the thorium chlorides in the LiCl-KCl eutectic as a function of temperature and composition must be known. The activity coefficient of ThCl$_4$ in KCl-LiCl relative to pure solid ThCl$_4$ was determined for various compositions and temperatures by measuring the electromotive force (e.m.f.) of the cell

$$\text{Th/ThCl}_4\text{,LiCl-KCl//LiCl-KCl,3.3wt.\% AgCl/Ag} \qquad (18)$$
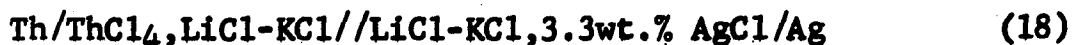
as a function of temperature and of ThCl$_4$ concontration. The

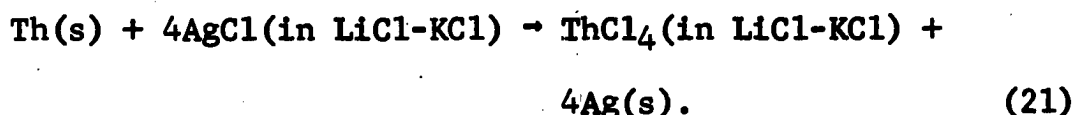compositions studied varied from 0.1 to 32.4 wt.% $ThCl_4$, and the temperature ranged from 450 to 650°C. The starting weight of LiCl-KCl eutectic in the tantalum crucible amounted to 500-600 grams. It is assumed that the reaction occurring at the thorium electrode in this cell may be represented as

$$Th(s) + 4Cl^- \rightarrow ThCl_4(in\ LiCl-KCl) + 4e^- \qquad (19)$$
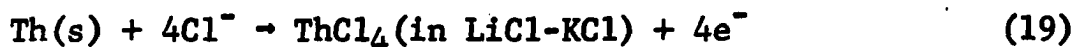
and that at the silver electrode as

$$4AgCl(in\ LiCl-KCl) + 4e^- \rightarrow 4Ag(s) + 4\ Cl^-. \qquad (20)$$

Therefore the overall reaction may be written

$$Th(s) + 4AgCl(in\ LiCl-KCl) \rightarrow ThCl_4(in\ LiCl-KCl) +$$
$$4Ag(s). \qquad (21)$$

The e.m.f. of Reaction 21 may be expressed as

$$E_{meas} = E^O_{ThCl_4} - E^O_{AgCl} - \frac{RT}{4F} \ln a_{ThCl_4} + \frac{RT}{F} \ln a_{AgCl}$$
$$+ E_{Ag-Ta} \qquad (22)$$

where

E^O = standard e.m.f. for the pure solid chloride

R = universal gas constant

T = temperature, °K

F = Faraday's constant

A = activity = $N\gamma$ = (mole fraction)(activity coefficient)

E_{Ag-Ta} = thermal e.m.f. generated between silver and tantalum electrodes.

All the quantities on the right-hand side of Equation 22 are known except a_{ThCl_4}; therefore, by measuring the e.m.f. as a function of mole fraction $ThCl_4$ in the salt and of temperature, the activity coefficient of $ThCl_4$ in the salt relative to pure solid $ThCl_4$ may be obtained as a function of concentration and temperature.

In Table 8 are listed, along with their respective references, the known quantities used in Equation 22 to calculate γ_{ThCl_4}.

Table 8. Quantities used in Equation 22 to calculate γ_{ThCl_4}

Quantity (in volts)	Value	Investigator	Ref. number
$E^{o}_{ThCl_4}$	$3.009-6.776\times10^{-4}T^{o}K$	This work	
E^{o}_{AgCl}	$1.126-2.920\times10^{-4}T^{o}K$	Yang and Hudson	17
$RT/3 \ln a_{AgCl}$ (for N_{AgCl} = 1.319×10^{-2})	$.0396-3.761\times10^{-4}T^{o}K$	Yang and Hudson	17
E_{Ag-Ta}	$-.0011+.041\times10^{-4}T^{o}K$	Gray	25

Equation 22 may be rearranged to give:

$$\log \gamma^{(s)}_{ThCl_4} = \log N_{ThCl_4} + \frac{4 \Im}{2.3RT}\left[E^{o}_{ThCl_4} - E^{o}_{AgCl} + \frac{RT}{\Im}\ln a_{AgCl} + E_{Ag-Ta} - E_{meas.}\right] \qquad (23)$$
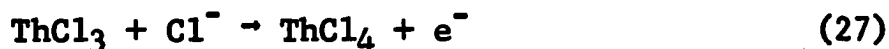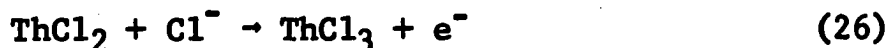
or, substituting the appropriate values of Table 8 into

Equation 23:

$$\log \gamma_{ThCl_4}^{(s)} = \log N_{ThCl_4} + \frac{4 \mathfrak{F}}{2.3RT} \left[1.9213 - 7.576 \times 10^{-4}T^{\circ}K - E_{meas.} \right] . \quad (24)$$

In Tables 9 and 10 are tabulated the e.m.f.'s of experiments

3-93-8 and 3-101-9 at various temperatures and compositions

as well as the activity coefficients of $ThCl_4$ calculated from

Equation 24.

In light of the phase diagram work, reduction of the

$ThCl_4$ in the salt by the thorium electrode must be considered.

It is possible that at the thorium electrode, the following

sequence of reactions occur:

$$Th + 2Cl^- \rightarrow ThCl_2 + 2e^- \quad (25)$$

$$ThCl_2 + Cl^- \rightarrow ThCl_3 + e^- \quad (26)$$

$$\underline{ThCl_3 + Cl^- \rightarrow ThCl_4 + e^-} \quad (27)$$

or, overall, $Th + 4Cl^- \rightarrow ThCl_4 + 4e^-. \quad (28)$

If this be the case, then Equation 21 does indeed represent

the cell reaction and Equations 22-24 are valid. It is with

reservation, however, that these activity coefficients are

calculated.

It may be noted here that γ_{ThCl_4} relative to pure liquid

$ThCl_4$ may be calculated from the above values through the

Table 9. Data for the cell Th/ThCl$_4$-LiCl-KCl//LiCl-KCl-3.3 wt.% AgCl/Ag*
(Experiment 3-93-8)

Total ThCl$_4$ added (gms.)	Wt.% Th nominal	Wt.% Th analysis	Sample weight (gms)	Wt.% ThCl$_4$	N$_{ThCl_4}$	T°C	E$_{meas}$ (volts)	-log γ(s)$_{ThCl_4}$	γThCl$_4$ x10^{+3}
0.56	.0645	--	--	0.106	1.75x10^{-4}	501.5	1.6033	3.252	0.560
1.17	0.135	0.13	2.12	0.209	3.45x10^{-4}	500.8	1.5916	3.223	0.598
2.26	0.282	0.26	2.14	0.419	6.92x10^{-4}	492.1	1.5845	3.242	0.573
					"	501.0	1.5801	3.218	0.606
					"	555.0	1.5512	3.082	.828
					"	583.5	1.5330	3.018	.960
					"	638.5	1.5057	2.904	1.248
4.04	0.47	0.455	2.18	0.733	1.21x10^{-3}	505.5	1.5679	3.208	.620
8.49	1.01	0.98	2.16	1.571	2.62x10^{-3}	501.3	1.5561	3.184	.655
10.85	1.27	1.28	2.21	2.062	3.45x10^{-3}	500.9	1.5524	3.200	.632
					"	504.2	1.5502	3.190	.646
					"	577.9	1.5070	2.998	1.006
					"	585.2	1.5030	2.981	1.045
					"	640.2	1.4704	2.860	1.380
28.68	3.26	3.24	1.98	5.220	8.98x10^{-3}	505.1	1.5314	3.114	.770

*Initial weight of LiCl-KCl eutectic was 527.8 grams

Table 10. Data for the cell Th/ThCl$_4$-LiCl-KCl//LiCl-KCl-3.3 wt.% AgCl/Ag*
(Experiment 3-101-9

Total ThCl$_4$ added (gms.)	Wt.% Th nominal	Wt.% Th analysis	Sample weight (gms.)	Wt.% ThCl$_4$	N_{ThCl_4}	T$^{\circ}$C	E_{meas} (volts)	$-\log$ (s) γ_{ThCl_4}	γ_{ThCl_4} x10^3
36.46	4.14	4.15	2.44	6.68	1.057×10^{-2}	440.0	1.5655	3.245	.569
					"	450.0	1.5608	3.214	.612
					"	473.8	1.5446	3.143	.720
					"	491.5	1.5352	3.093	.807
					"	511.8	1.5219	3.038	.917
					"	540.0	1.5048	2.967	1.079
					"	540.4	1.5040	2.966	1.082
					"	574.0	1.4831	2.888	1.294
					"	595.0	1.4710	2.842	1.440
					"	620.6	1.4548	2.789	1.626
					"	646.7	1.4393	2.738	1.828
102.74	10.50	10.57	2.80	17.05	2.97×10^{-2}	450.1	1.5413	3.177	.665
					"	455.0	1.5397	3.161	.690
					"	456.0	1.5384	3.158	.695
					"	485.2	1.5208	3.067	.857
					"	497.4	1.5110	3.031	.932
					"	525.4	1.4938	2.953	1.114
					"	546.3	1.4808	2.898	1.265
					"	568.1	1.4649	2.844	1.432
					"	601.0	1.4454	2.767	1.710
					"	608.9	1.4400	2.750	1.778
					"	649.3	1.4148	2.664	2.170

*Initial weight of LiCl-KCl eutectic was 509.9 grams.

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Table 10.   (Continued)

Total ThCl$_4$ added (gms.)	Wt.% Th nominal	Wt.% Th analysis	Sample weight (gms.)	Wt.% ThCl$_4$	N$_{ThCl_4}$	T$^{\circ}$C	E$_{meas}$ (volts)	$-\log(s)$ γ_{ThCl_4}	γ_{ThCl_4} x10^3
166.23	15.10	14.90	24.35	24.00	4.51x10^{-2}	448.2	1.5342	3.054	.883
						454.1	1.5263	3.037	.918
						485.4	1.5083	2.956	1.107
						498.6	1.4999	2.923	1.193
						523.7	1.4849	2.865	1.364
						546.7	1.4705	2.814	1.534
						555.1	1.4610	2.796	1.600
						584.9	1.4445	2.736	1.837
						602.3	1.4347	2.702	1.987
						619.9	1.4234	2.670	2.139
						652.7	1.4009	2.613	2.440
241.7	20.2	20.1	2.61	32.4	6.65x10^{-2}	451.2	1.5200	2.924	1.192
					"	480.7	1.5011	2.846	1.426
					"	501.0	1.4865	2.795	1.603
					"	510.8	1.4808	2.772	1.691
					"	541.3	1.4614	2.702	1.986
					"	568.3	1.4436	2.645	2.265
					"	595.0	1.4246	2.592	2.560
					"	627.3	1.4053	2.532	2.940
					"	656.6	1.3857	2.482	3.298

relationship

$$\log \gamma_{ThCl_4}^{(\ell)} = \log \gamma_{ThCl_4}^{(s)} - \frac{\Delta H_{fus,ThCl_4}}{2.3RT} \frac{(T_{fus}-T)}{T_{fus}} \qquad (29)$$

where superscripts (ℓ) and (s) denote liquid and solid reference states respectively and ΔH_{fus} and T_{fus} are the heat of fusion and melting point of $ThCl_4$. Substituting the values of 14,690 calories for ΔH_{fusion} and $1043^{\circ}K$ for T_{fusion} measured in this laboratory by G. J. Gartner (26) into Equation 29 gives the following relationship between the two γ's:

$$\text{Log } \gamma_{ThCl_4}^{(\ell)} = \log \gamma_{ThCl_4}^{(s)} + 3.078 - \frac{3212}{T} . \qquad (30)$$

The measured e.m.f.'s as a function of temperature for the various compositions are presented in Figure 6. These e.m.f.'s were fitted by a least squares treatment to an equation of the type $E = a + bT^{\circ}K$. Substitution of these expressions into Equation 24 leads to equations for $\log \gamma_{ThCl_4}^{(s)}$ at various compositions of the form $\log \gamma_{ThCl_4}^{(s)} = (c/T) + d$. The results of these calculations are given in Table 11.

These results agree well with the few measurements that Yang and Hudson (9) made for this system in the temperature range of $500-550^{\circ}C$. For example they found for N_{ThCl_4} values of 4.8×10^{-4}, 1.90×10^{-3}, and 3.77×10^{-3} at $500^{\circ}C.$, γ_{ThCl_4} values of 0.71×10^{-3}, 0.79×10^{-3}, and 1.18×10^{-3}

Figure 6. Electromotive force in volts of cell $Th/ThCl_4$, $LiCl$-KCl//$LiCl$-KCl, $AgCl/Ag$ as a function of temperature (^OC) for various compositions of $ThCl_4$ in the salt (see Tables 9 and 10)
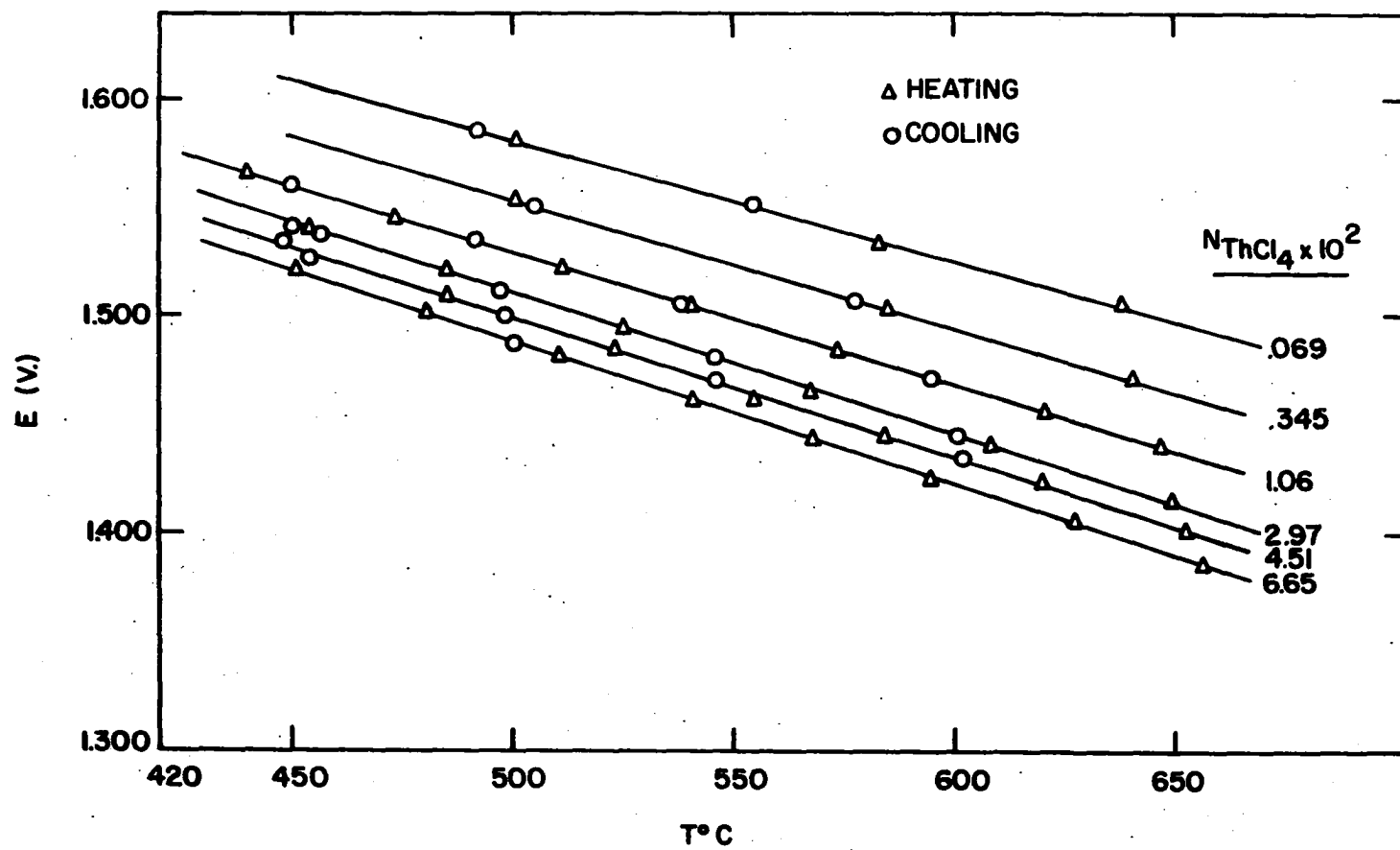
respectively. For the same mole fractions the values of

γ_{ThCl_4} at $500^{\circ}C$ found in this study would be 0.60, 0.63 and

0.66×10^{-3} respectively.

Table 11. Least squares equations for measured e.m.f.'s and resulting equations for $\log \gamma_{ThCl_4}^{(s)}$

N_{ThCl_4}	E(volts)	$\log \gamma_{ThCl_4}^{(s)}$
6.92×10^{-4}	$2.001 - 5.444 \times 10^{-4}T$	$-1609/T - 1.139$
3.45×10^{-3}	$2.007 - 5.872 \times 10^{-4}T$	$-1722/T - .975$
1.057×10^{-2}	$2.001 - 6.106 \times 10^{-4}T$	$-1609/T - .988$
2.97×10^{-2}	$2.006 - 6.420 \times 10^{-4}T$	$-1716/T - .804$
4.51×10^{-2}	$1.993 - 6.383 \times 10^{-4}T$	$-1438/T - 1.060$
6.65×10^{-2}	$1.993 - 6.535 \times 10^{-4}T$	$-1450/T - .922$

One can see from the values of γ_{ThCl_4} in Tables 9 and 10

that the temperature dependence of γ_{ThCl_4} is not very large.

This has been found by Flengas and Ingraham (27) to be the

case for many metal chlorides in fused salt systems. They

interpreted this phenomenon as meaning that the extent of com-

plex formation in the salt is not very temperature-dependent.

The activity coefficient of $ThCl_3$ in the LiCl-KCl eutec-

tic relative to the pure solid should be about the same as

that of UCl_3 since their ionic radii are very nearly the same

(28): 1.14 angstroms for Th^{+3} as compared with 1.11 angstroms for U^{+3}. This similarity of activity coefficients of UCl_3 and $ThCl_3$ has been borne out in work by Parry and Chiotti (7) who obtained data which indicated that the ratio of the activity coefficients of UCl_3 and $ThCl_3$ in the eutectic was very close to one. The activity coefficient of UCl_3 in LiCl-KCl has been found to be very nearly unity (29,30) in the temperature range of interest in this study (500-700°C); therefore a value of one will be used for the activity coefficient of $ThCl_3$ in this investigation.

Attempts were made to determine the activity coefficient of $ThCl_2$ relative to the pure solid in the LiCl-KCl eutectic. It was anticipated that $ThCl_2$ would be relatively insoluble in the LiCl-KCl eutectic since $ZrCl_2$ has been found to be very insoluble in this salt (4,21,22) and thorium often behaves in its chemistry like zirconium. According to the free energy data in Table 1, the chief product obtained upon equilibration of $ThCl_4$ in LiCl-KCl with thorium metal should be $ThCl_2$, the reaction being

$$ThCl_4(\text{in LiCl-KCl}) + Th \rightarrow 2ThCl_2\downarrow . \qquad (31)$$

It was thought, therefore, that if solutions of $ThCl_4$ in LiCl-KCl were equilibrated with thorium metal, the final salt

analysis should represent the solubility limit of $ThCl_2$ in the salt. At saturation, the activity of $ThCl_2$ will be one and since

$$a_{ThCl_2} = N_{ThCl_2} \gamma_{ThCl_2}, \tag{32}$$

γ_{ThCl_2} can be calculated from the mole fraction of $ThCl_2$. However, when experiments of this type were attempted, the thorium metal was found to have become coated with a gray-black film, probably $ThCl_2$, and the thorium content of the salt was found to have changed only slightly from the initial value. Table 12 gives the experimental data for these experiments. The weight of unreacted thorium was obtained by washing, drying, and weighing the thorium which remained after equilibration. The difference between the initial amount of thorium and the amount of thorium remaining in these experiments can not be accounted for by the increase in thorium content of the salt alone. This could be due to a failure to find and weigh all of the unreacted thorium but is probably due to the precipitation of $ThCl_2$.

It will be assumed that Reaction 31 did not go to completion, but that the equilibrium

$$ThCl_4 + ThCl_2 \rightleftharpoons 2ThCl_3 \tag{33}$$

is attained, where $ThCl_2$ is an insoluble precipitate on the

Table 12. Data for equilibrations of $ThCl_4$ in LiCl-KCl with thorium

Experi-ment	Initial charge (gms.)			Initial wt.% Th based on $ThCl_4$ added	Heat* treatment	Final salt analysis wt.% Th	Wt. unreacted thorium (gms.)
	LiCl-KCl	$ThCl_4$	Th				
3-152-1	30.170	0.770	0.853	1.55	700°C-26hrs.	1.60	0.756
4-5-2	33.794	1.084	0.916	1.93	700°C-48hrs.	1.95	0.701
4-8-1	29.197	1.045	1.129	2.11	700°C-30hrs.	2.24	0.940
3-151-1	29.950	0.700	0.575	1.41	700°C-24hrs.	1.58	0.231
3-151-2	30.386	1.398		2.73	800°C-26hrs.	2.89	0.674

*Water-quenched.

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surface of the thorium metal. With these assumptions, calculations of γ_{ThCl_2} can be made. It can be shown, that under these conditions,

$$N_i - N_{Th,R} = N_{ThCl_4} + \tfrac{1}{2}\sqrt{10^{-3}\,N_{ThCl_4}} \tag{34}$$

and $\quad N_{ThCl_2} = N_{ThCl_4} - 2N_i + 2N_{Th,R} + N_{Th} \tag{35}$

where N_i = initial mole fraction of $ThCl_4$ in the salt

$\quad N_{Th,R}$ = number of moles of thorium reacted divided by total number of moles of salt

$\quad N_{Th}$ = total mole fraction of thorium at equilibrium

N_{ThCl_4} = mole fraction of $ThCl_4$ in the salt at equilibrium

and

N_{ThCl_2} = mole fraction of $ThCl_2$ in the salt at equilibrium.

The derivations of these two equations are given in Appendix A. Thus from the experimental data and Equations 34 and 35, N_{ThCl_2} can be calculated. From N_{ThCl_2}, γ_{ThCl_2} can be calculated since

$$N_{ThCl_2}\gamma_{ThCl_2} = 1 \tag{36}$$

The results of these calculations are given in Table 13. The scatter in the calculated values of γ_{ThCl_2} is quite large. It would appear from these data that γ_{ThCl_2} at 700°C is about 1×10^3.

Table 13. Results of calculations of γ_{ThCl_2} from equilibrations of $ThCl_4$ in LiCl-KCl with thorium in Table 12

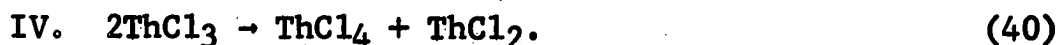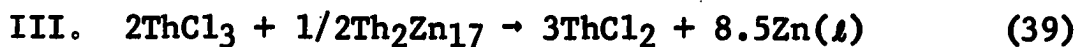| Experiment	T^oC	Initial mole fraction $ThCl_4, N_1$	Moles thorium reacted $=N_{Th,R}$	Total mole fraction thorium, N_{Th}	N_{ThCl_2}	γ_{ThCl_2}
3-152-1	700	3.80×10^{-3}	0.773×10^{-3}	3.95×10^{-3}	0.09×10^{-3}	1.11×10^4
4-5-2	700	4.78×10^{-3}	1.52×10^{-3}	5.00×10^{-3}	0.92×10^{-3}	1.09×10^3
4-8-1	700	5.33×10^{-3}	1.55×10^{-3}	6.45×10^{-3}	1.74×10^{-3}	5.75×10^2
3-151-1	700	3.48×10^{-3}	2.76×10^{-3}	3.84×10^{-3}	2.79×10^{-3}	3.94×10^2
3-151-2	800	6.86×10^{-3}	1.15×10^{-3}	7.02×10^{-3}	0.10×10^{-3}	1.0×10^4

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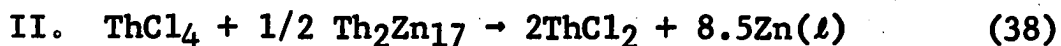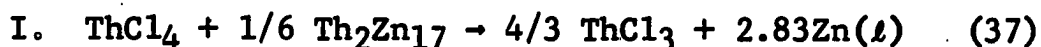
In an attempt to determine γ_{ThCl_2} in another manner, a solution of 5.26 grams of $ThCl_4$ in 32.92 grams of the LiCl-KCl eutectic was equilibrated with a large excess of thorium metal shavings (21.49 grams). These shavings were packed into one end of the tantalum crucible so that when the crucible was tipped upside down, the shavings remained in place. This mixture was equilibrated at 700^OC for 17 hours in a rocking furnace. The charge was then settled upside down for $1\frac{1}{2}$ hours at 700^OC to separate the salt solution from the metal. The thorium content of the salt was found to have increased to 8.84 wt.% Th from an initial concentration of 8.53 wt.% Th. The thorium shavings, which were covered with gray-black material, were removed from the crucible in a dry box and placed into another tantalum crucible which contained 23.20 grams of the LiCl-KCl eutectic. This charge was then equilibrated at 700^OC for 10 hours. If enough $ThCl_2$ had formed on the surface of the metal in the initial equilibration to still saturate this salt, the final analysis of this salt should be representative of the solubility limit of $ThCl_2$ in LiCl-KCl at 700^OC. The final salt analysis was 0.318 wt.% Th. This amount of thorium in the salt as $ThCl_2$ represents a mole fraction of $ThCl_2$ of 7.75×10^{-4}. If the solution is indeed

saturated with $ThCl_2$, this value gives 1.29×10^3 for γ_{ThCl_2} at $700^\circ C$ in the LiCl-KCl eutectic. This value is within the range of values calculated in Table 13; therefore for this investigation 1×10^3 for γ_{ThCl_2} at $700^\circ C$ will be used. Since at $500^\circ C$, the solubility of $ThCl_2$ in the salt should be lower than it is at $700^\circ C$, 1×10^4 will be used for γ_{ThCl_2} at $500^\circ C$.

Equilibria between Solutions Consisting of $ThCl_4$ in LiCl-KCl and Th_2Zn_{17} in Zinc

Calculations of the extent of reduction of $ThCl_4$ by the thorium-zinc alloy in the LiCl-KCl-liquid zinc system can be made from the free energy data for the thorium-zinc alloy and the thorium chlorides and the activity coefficients of the thorium chlorides in the salt. In the LiCl-KCl-liquid zinc system, there are four possible reactions that may be written involving thorium chlorides and the thorium-zinc alloy:

$$I. \quad ThCl_4 + 1/6\ Th_2Zn_{17} \rightarrow 4/3\ ThCl_3 + 2.83Zn(\ell) \quad (37)$$

$$II. \quad ThCl_4 + 1/2\ Th_2Zn_{17} \rightarrow 2ThCl_2 + 8.5Zn(\ell) \quad (38)$$

$$III. \quad 2ThCl_3 + 1/2Th_2Zn_{17} \rightarrow 3ThCl_2 + 8.5Zn(\ell) \quad (39)$$

$$IV. \quad 2ThCl_3 \rightarrow ThCl_4 + ThCl_2. \quad (40)$$

However, it can be shown that these four relations represent only two independent equilibria. Furthermore, at equilibrium,

$$N_{Th} = N_{ThCl_4} + N_{ThCl_3} + N_{ThCl_2}$$

$$= N_{ThCl_4} + \left(\frac{K_I}{K_{\gamma I}}\right)^{3/4} N_{ThCl_4}^{3/4} + \left(\frac{K_{II}}{K_{\gamma II}}\right)^{\frac{1}{2}} N_{ThCl_4}^{\frac{1}{2}} \qquad (41)$$

where N = mole fraction

K_i = equilibrium constant for reaction i

$K_{\gamma i}$ = activity coefficient ratio for reaction i

The derivation of Equation 41 is given in Appendix B.

From Equation 41, the free energy data for Reactions I and II, and the activity coefficients of the thorium chlorides in the salt, the mole fractions of $ThCl_4$, $ThCl_3$, and $ThCl_2$ that should be present at equilibrium can be calculated as a function of the total mole fraction of thorium. It should be noted here that shifting of the equilibria towards the lower chlorides is favored by dilute solutions. If K_γ is a constant, which should be a fairly good assumption for dilute solutions, then K_N is also a constant. K_N of Reaction I may be written

$$K_N = \frac{n_{ThCl_3}^{4/3}}{n_{ThCl_4}} \frac{1}{(\sum n)^{1/3}} \qquad (42)$$

where n denotes number of moles. Thus as $\sum$n, the total number of moles of thorium chlorides plus LiCl-KCl eutectic increases, the number of moles of $ThCl_4$ must decrease (with a corresponding increase in the number of moles of $ThCl_3$). The same

argument applies for Reaction II.

In Table 14 are listed, for 500 and 700°C, the standard free energy values for the compounds involved in Reactions I and II, the equilibrium constants for these reactions, and the calculated K ratios appearing in Equation 41.

Table 14. Free energy data and equilibrium constants for Reactions I and II at 500° and 700°C

T^oC	$\Delta F^o_{ThCl_4}$ kcal	$\Delta F^o_{ThCl_3}$ kcal	$\Delta F^o_{ThCl_2}$ kcal	$\Delta F^o_{Th_2Zn_{17}}$ kcal	$\dfrac{K_I}{K_{\gamma I}}$	$\dfrac{K_{II}}{K_{\gamma II}}$
500	-229.2	-187.8	-144.8	-89.5	8.6×10^{-2}	1.63×10^{-8}
700	-216.7	-178.0	-139.3	-75.1	10×10^{-2}	3.1×10^{-6}

The values of the ratio $K_{II}/K_{\gamma II}$ indicate that not much $ThCl_2$ should be present at equilibrium. The ratio N_{ThCl_3}/N_{ThCl_4} at 500 and 700°C was calculated as a function of total mole fraction of thorium in the salt and is plotted in Figures 7 and 8 for these two temperatures.

Experiments were done involving batch-type equilibrations between various initial compositions of $ThCl_4$ in the LiCl-KCl eutectic salt and an excess of the zinc-10% thorium alloy at 500 and 700°C. The initial charges and the thermal history of the equilibrations are presented in Tables 15 and 16. The 500°C equilibrations were rocked approximately twenty-four

Figure 7. Theoretical and experimental N_{ThCl_3}/N_{ThCl_4} ratio at 500^oC as a function of total thorium mole fraction at equilibrium. See Table 15
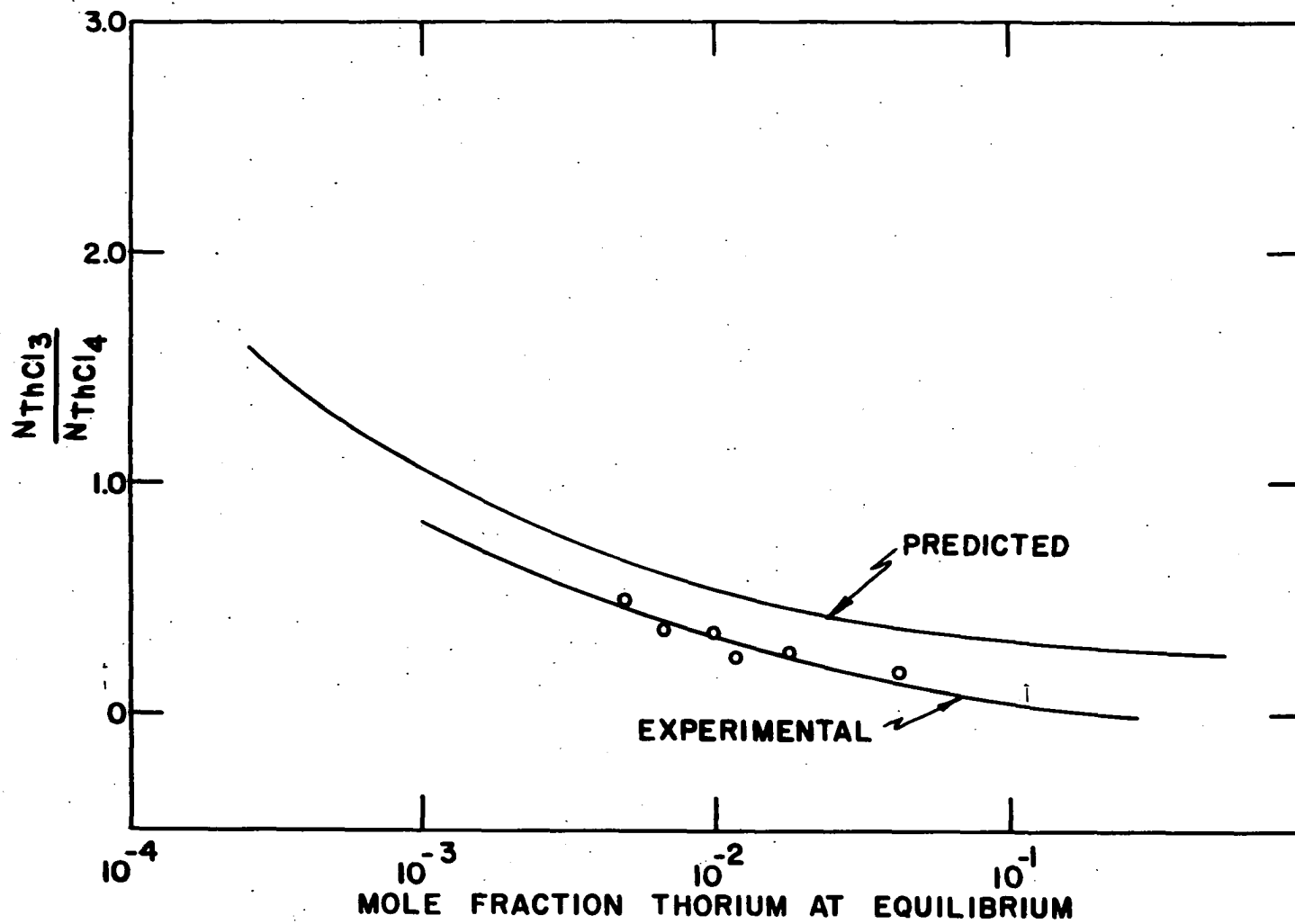
Figure 8. Theoretical and experimental N_{ThCl_3}/N_{ThCl_4} ratio at $700^{\circ}C$ as a function of total thorium mole fraction at equilibrium. See Table 16
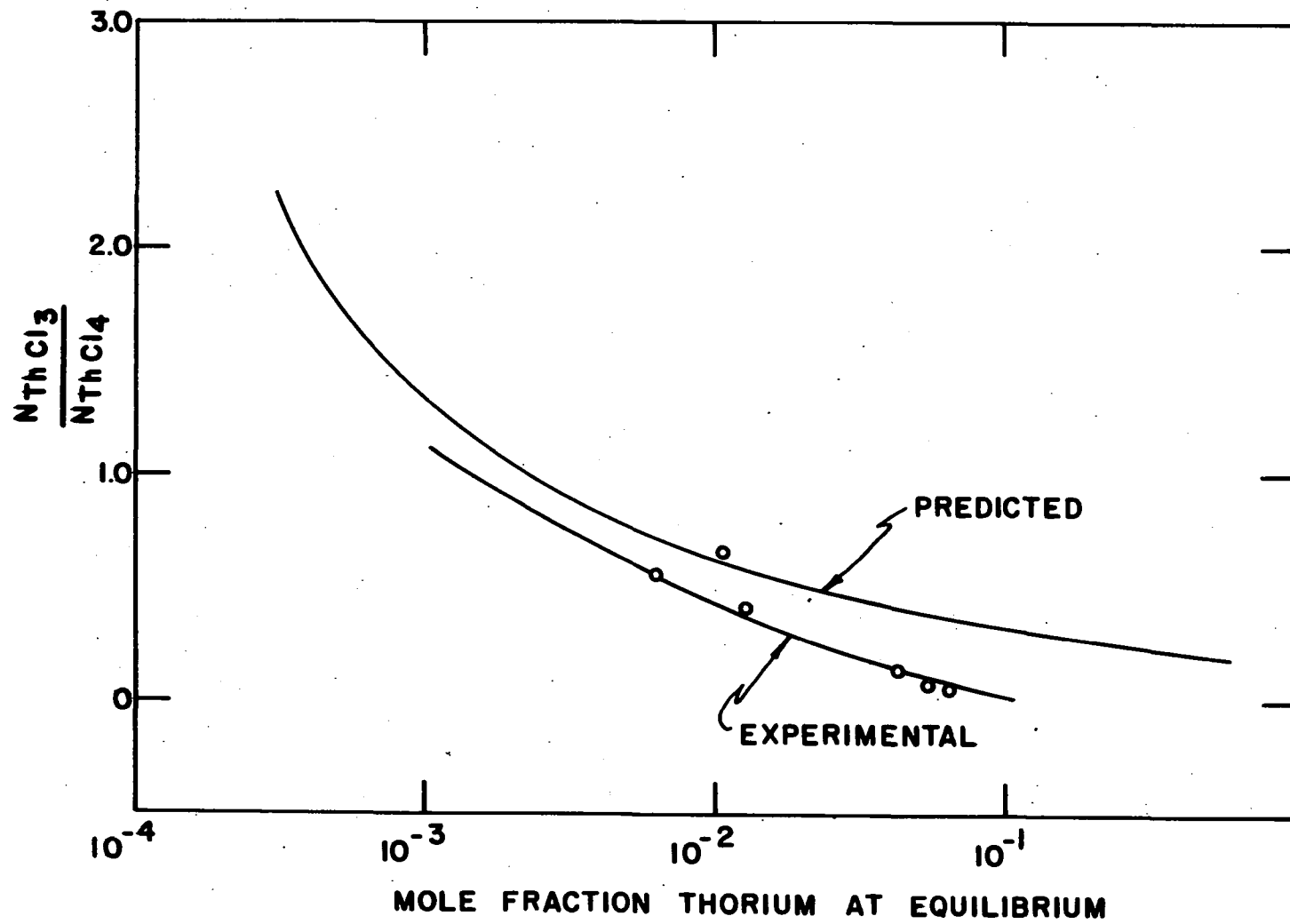
Table 15. Initial weights, thermal history, and resulting analyses of batch equilibrations of salt with excess Zn-10 wt.% Th alloy at 500°C

Initial charge gms.	Initial wt.% $ThCl_4$	Thermal history*	Final wt.% Th	N_{Th} final	N_{ThCl_3}/N_{ThCl_4}	$K_N = \dfrac{N_{ThCl_3}^{4/3}}{N_{ThCl_4}}$
56.49 salt 55.7 alloy	3.00(1.86% Th)	21 hrs.R 1½ hrs.S	2.025	4.94×10^{-3}	.492	.0578
53.26 salt 54.5 alloy	4.05(2.51% Th)	20 hrs.R 2 hrs.S	2.69	6.7×10^{-3}	.352	.0444
46.88 salt 46.3 alloy	5.75(3.56% Th)	24 hrs.R 2½ hrs.S	3.81	9.63×10^{-3}	.343	.0463
48.44 salt 49.8 alloy	6.90(4.28% Th)	36 hrs.R 2 hrs.S	4.54	1.16×10^{-2}	.299	.0414
47.12 salt 45.4 alloy	10.43(6.46% Th)	21½ hrs.R 1½ hrs.S	6.82	1.80×10^{-2}	.266	.0414
19.54 salt 17.3 alloy	21.90(13.60% Th)	23 hrs.R 4½ hrs.S	14.18	4.2×10^{-2}	.184	.0344

*R = rocking, S = settling.

Table 16. Initial weights, thermal history, and resulting analyses of batch equilibrations of salt with excess Zn-10 wt.% Th alloy at 700°C

Initial charge gms.	Initial wt.% $ThCl_4$	Thermal history*	Final wt.% Th	N_{Th} final	N_{ThCl_3}/N_{ThCl_4}	$K_N = \dfrac{N_{ThCl_3}^{4/3}}{N_{ThCl_4}}$
21.27 salt 20.4 alloy	3.81(2.36% Th)	24 hrs.R 24 hrs.S	2.54	6.30×10^{-3}	.563	.074
21.40 salt 22.2 alloy	6.07(3.76% Th)	24 hrs.R 2 hrs.S	4.20	1.07×10^{-2}	.667	.1084
21.66 salt 22.2 alloy	7.32(4.54% Th)	24 hrs.R 16 hrs.S	5.01	1.29×10^{-2}	.492	.0798
17.60 salt 21.2 alloy	22.60(14.02% Th)	12 hrs.R 1 hr.S	14.50	4.32×10^{-2}	.149	.0265
17.86 salt 36.7 alloy	27.30(16.94% Th)	16 hrs.R 2 hrs.S	17.26	5.42×10^{-2}	.075	.0117
16.18 salt 22.4 alloy	30.70(19.05% Th)	16 hrs.R 2 hrs.S	19.42	6.36×10^{-2}	.053	.0078

*R = rocking, S = settling.

67

hours at 700°C before being given the heating treatment at 500°C indicated in Table 15.

The chemical analyses of the salts resulting from the 500 and 700°C equilibrations are also given in their respective tables. From the known weights of starting materials and the final salt analyses, the ratio N_{ThCl_3}/N_{ThCl_4} was calculated. These calculated ratios are presented in the tables and are also plotted on Figures 7 and 8 for comparison with the values of the predicted ratios. It should be noted here that thorium is insoluble in this salt at the temperatures being considered here; therefore any thorium found in the salt must be present as thorium chloride. This agreement indicated that the thermodynamic data used to calculate these ratios are reasonably accurate and that, indeed, $ThCl_4$ and $ThCl_3$ are the predominent thorium chlorides in solution when the salt is in equilibrium with the thorium-zinc alloy.

Study of the Cell $Th/LiCl-KCl-ThCl_x/Th_2Zn_{17}$ in Zinc

In an attempt to observe the change in relative amounts of $ThCl_4$ and $ThCl_3$ with changes in the total thorium concentration in the salt, the e.m.f. between a thorium electrode and a zinc solution saturated with Th_2Zn_{17} was measured at

various thorium concentrations in the salt. It was anticipated that the measured e.m.f.'s should give some information as to the oxidation state of thorium in the salt since the half-cell reactions occurring should be

$$Th + xCl^- \rightarrow ThCl_x + Xe^- \tag{43}$$

and

$$ThCl_x + 8.5Zn + Xe^- \rightarrow \tfrac{1}{2}Th_2Zn_{17}. \tag{44}$$

Therefore the measured e.m.f. of the cell should be related to the standard free energy of formation of Th_2Zn_{17} by the expression

$$\tfrac{1}{2}\Delta F^O_{Th_2Zn_{17}} = - X\mathcal{F}E . \tag{45}$$

Thus from the measured e.m.f. of the cell and the known values of $\Delta F^O_{Th_2Zn_{17}}$, the average oxidation state of the thorium in the salt should be obtained. Table 17 gives the experimental results of experiments 3-109-10. Figure 9 shows the resulting e.m.f.'s measured as a function of temperature at various thorium concentrations in the salt. The curves observed indicate χ to be about three at high concentrations of thorium in the salt and about four at low concentrations. This is just opposite to the expected trend discussed in the previous section. However, if the curves truly reflect a change in the oxidation state of thorium in the salt, this should also be reflected in the e.m.f. between the thorium

Table 17. Data and electromotive force measurements of cell Th ThCl$_x$-LiCl-KCl/Th$_2$Zn$_{17}$ in Zn (Experiment 3-109-10)

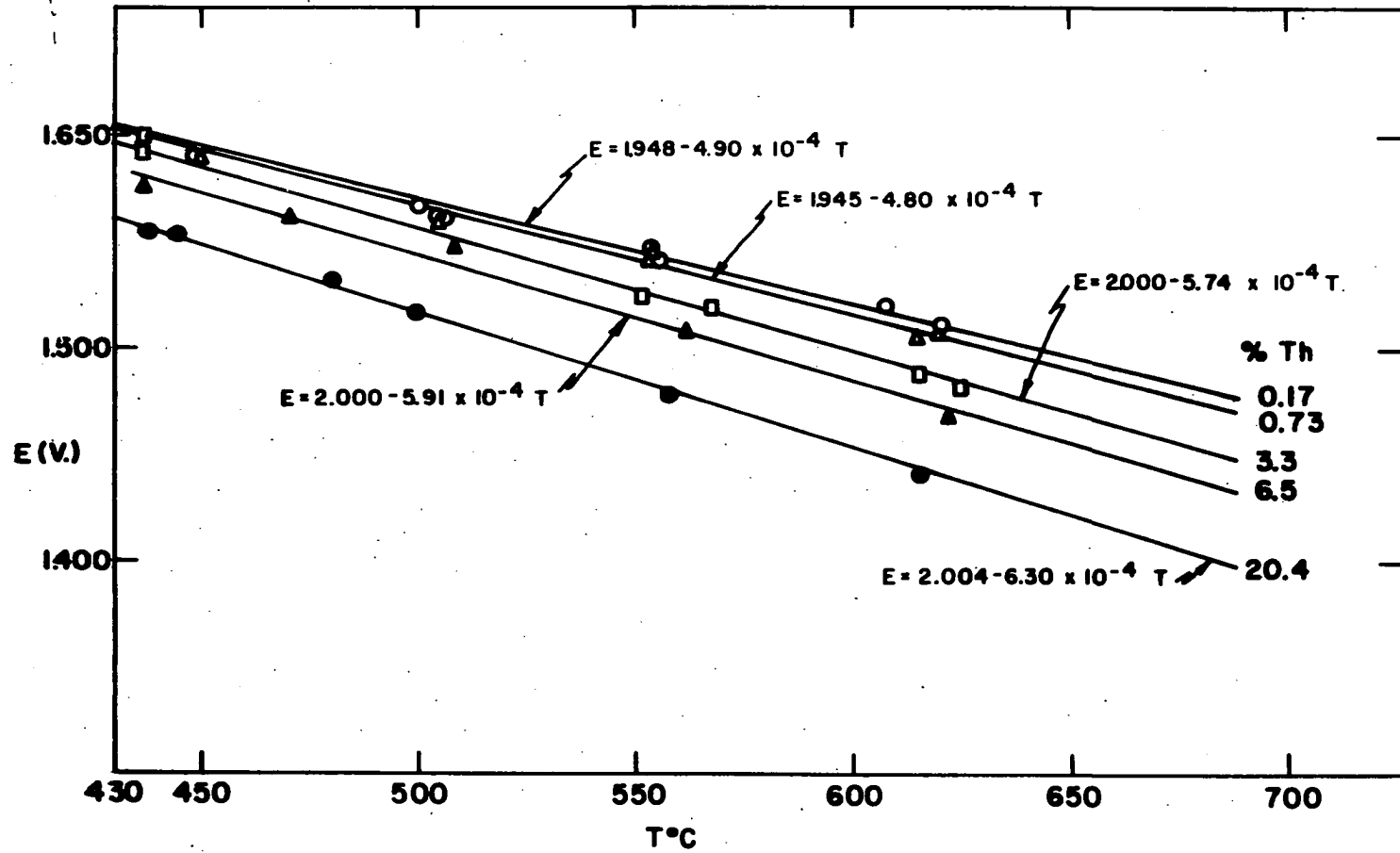| Total ThCl$_4$ added (gms)	Wt.% Th nominal	Wt.% Th analysis	Sample wt.(gms)	T^{o}C	E$_{meas}$ (volts)
0.431	.049	.009	2.74	453.6	.506
	"	.008	2.92	505.4	.439
	"	.009	3.19	556.8	.398
	"	.019	2.65	608.0	.390
	"	.054	3.29	652.4	.365
1.548	.181	.112	2.79	450.0	.523
	"	.178	2.87	504.1	.446
	"	.168	2.81	553.4	.425
	"	.185	2.68	620.3	.404
3.146	.372	.267	2.08	444.8	.525
	"	.276	2.76	499.0	.522
	"	.390	2.68	553.0	.419
	"	.316	2.55	619.0	.396
6.448	.760	.760	2.55	448.6	.509
	"	.728	2.74	504.4	.455
	"	.731	2.46	554.2	.438
	"	.683	2.27	615.7	.408
17.917	2.148	2.01	2.78	467.0	.514
	"	2.00	2.65	495.9	.476
	"	2.02	2.63	551.4	.429
	"	2.07	2.85	614.9	.408
30.779	3.70	3.36	5.21	436.4	.599
	"	3.23	2.73	470.0	.577
	"	3.27	5.30	507.0	.500
	"	3.25	2.79	538.7	.447
	"	3.24	5.52	567.1	.431
	"	3.32	5.98	624.7	.411
61.005	7.35	6.65	5.29	436.3	.605
	"	6.61	2.62	470.2	.596
	"	6.50	5.03	508.5	.532
	"	6.49	5.38	561.3	.502
	"	6.43	5.30	621.5	.510
221.10	20.4			444.2	.616
	"			499.6	.539
	"			557.4	.529
	"			615.4	.520

*Initial charge: 547 grams LiCl-KCl, 207 grams zinc-7.6 wt.% thorium alloy.

Figure 9. Electromotive force in volts of cell $Th/LiCl-KCl-ThCl_x/$
Th_2Zn_{17} in Zn as a function of temperature for various
thorium concentrations in the salt (see Table 17)
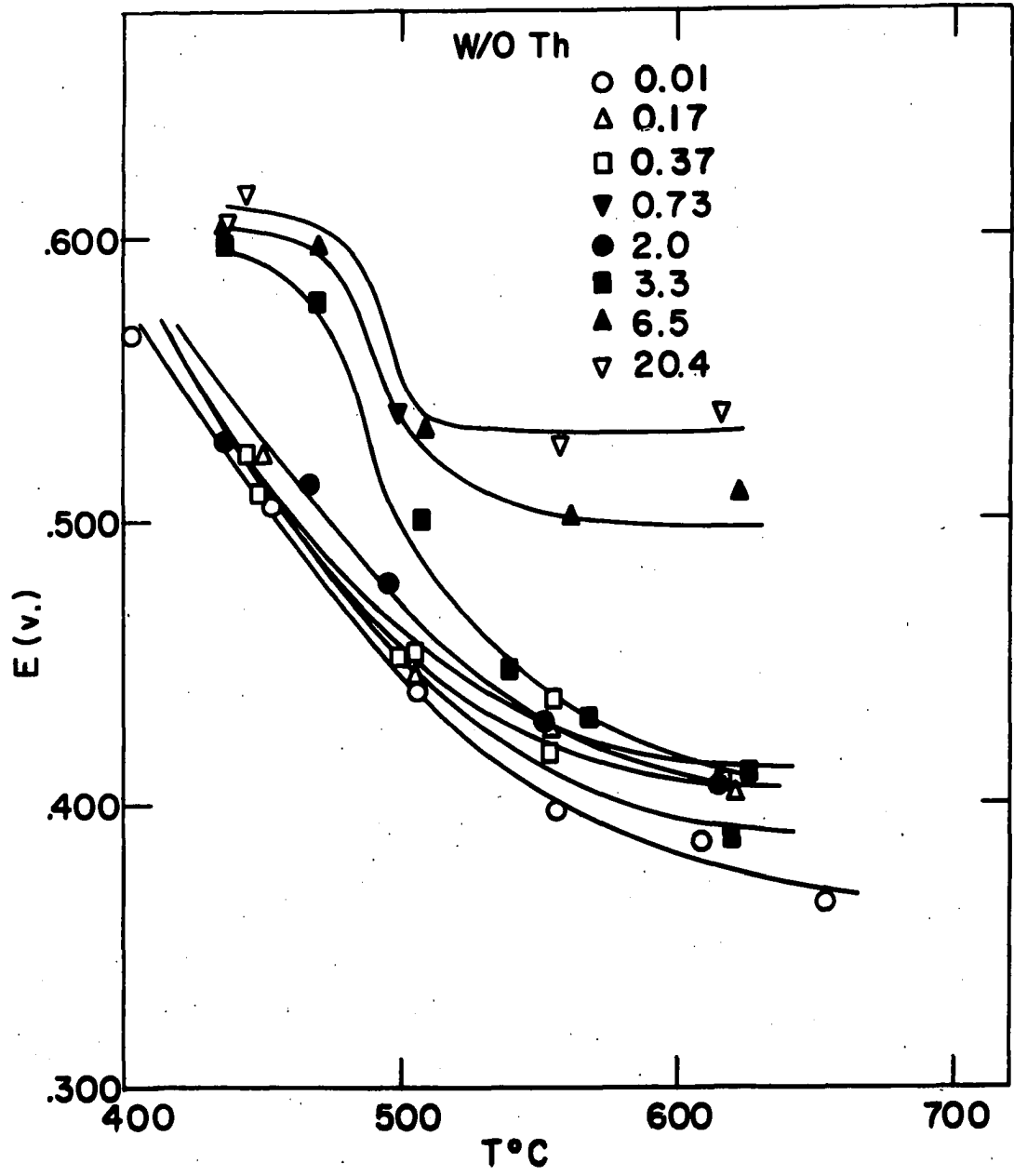
electrode and a silver-silver chloride reference electrode.
These e.m.f.'s were measured for the same thorium concentra-
tions and temperatures and are shown in Figure 10. The fact
that these e.m.f.'s give straight lines as a function of tem-
perature whereas the e.m.f.'s measured between the thorium and
the thorium-zinc electrodes show such a pronounced curvature
with temperature suggests that something was happening either
in the thorium-zinc alloy or at the salt-metal interface. In
an attempt to check whether or not something was happening in
the thorium-zinc alloy, a sample of the alloy was held at
500^OC for a week. No change could be detected in the micro-
structure of the alloy, indicating that the cause for the
observed variation in the e.m.f.'s measured between the thor-
ium and thorium-zinc electrodes did not lie in the alloy. In
this experiment, the thorium concentration in the salt did not
increase over the nominal composition based on $ThCl_4$ additions
as would be expected if the $ThCl_4$ were being reduced to lower
chlorides. In addition, the e.m.f.'s measured between the
thorium electrode and the silver-silver chloride reference
electrode at the various thorium concentrations are very close
to those measured for similar thorium concentrations when only
$ThCl_4$ was present in the salt such as in experiments 3-93-8

Figure 10. Electromotive force in volts of cell $Th/LiCl-KCl-ThCl_x/$ $LiCl-KCl-3.3$ wt.% AgCl Ag as a function of temperature for various thorium concentrations in the salt

$E = 1.948 - 4.90 \times 10^{-4} \, T$

$E = 1.945 - 4.80 \times 10^{-4} \, T$

$E = 2.000 - 5.74 \times 10^{-4} \, T$

$E = 2.000 - 5.91 \times 10^{-4} \, T$

$E = 2.004 - 6.30 \times 10^{-4} \, T$

% Th

0.17
0.73
3.3
6.5
20.4

E (V.)

1.650

1.500

1.400

430 450   500   550   600   650   700

T °C

75

and 3-101-9 (Tables 9 and 10). This indicates that something
at the salt-metal interface was inhibiting reduction of the
ThCl$_4$ by the alloy and also causing the anamolous e.m.f.'s
between the thorium and thorium-zinc electrodes.

When the experiment was concluded, the charge was sliced
vertically. A layer about 1/8" thick of gray material was
found between the metal and salt phases. This layer was prob-
ably composed of ThO$_2$ or ThOCl$_2$. This material was probably
the cause of the anamolous e.m.f.'s measured between the
thorium and thorium-zinc electrodes and also probably pre-
vented the reaction between the alloy and the ThCl$_4$ in the
salt.

Two other separate experiments were made using the cell
Th/LiCl-KCl-ThCl$_4$/Th$_2$Zn$_{17}$ in Zn but with very high initial
ThCl$_4$ concentrations. The ThCl$_4$ concentration was 32.4 wt.%
in the first experiment and 35.5 wt.% in the other. The
e.m.f.'s measured as a function of temperature are given in
Table 18.

These data were treated by a least squares method to
give the following equation for the temperature-dependence
of the measured electromotive force E, in volts:

$$E = 0.7927 - 3.974 \times 10^{-4} T^{\circ}K .$$

<div align="right">(46)</div>

This line and the experimental points are presented in Figure

11.

Table 18. Electromotive force in volts of cell $Th/ThCl_4$, $LiCl-KCl/Th_2Zn_{17}(s)$ in $Zn(l)$ as a function of temperature ($^\circ C$)

| Wt. % $ThCl_4$ in salt	$T^\circ C$	E(volts)
32.4[a]	445.3	0.5074
"	483.4	0.4892
"	515.1	0.4828
"	520.8	0.4736
"	552.4	0.4650
"	570.5	0.4542
"	594.9	0.4478
"	628.4	0.4330
"	648.5	0.4260
35.5[b]	450.2	0.5066
"	465.4	0.5000
"	494.0	0.4881
"	518.1	0.4780
"	519.2	0.4780
"	572.4	0.4582
"	601.4	0.4483
"	643.8	0.4291

[a]Initial charge: 249 gms. $ThCl_4$, 519 gms. LiCl-KCl, 200 gms. Zn-10 wt.% Th.

[b]Initial charge: 112 gms. $ThCl_4$, 200 gms. LiCl-KCl, 320 gms. Zn-10 wt.% Th.

From these data and the use of n = 4 in Equation 45, $\Delta F^\circ_{Th_2Zn_{17}}$ was found to have the following temperature dependence:

$$\Delta F^\circ_{Th_2Zn_{17}} = -146,300 + 73.3T \text{ calories/mole.} \quad (47)$$

Figure 11. Electromotive force in volts of cell Th/LiCl-KCl-34 wt.%
ThCl$_4$/Th$_2$Zn$_{17}$ in Zn as a function of temperature ($^{\circ}$C)
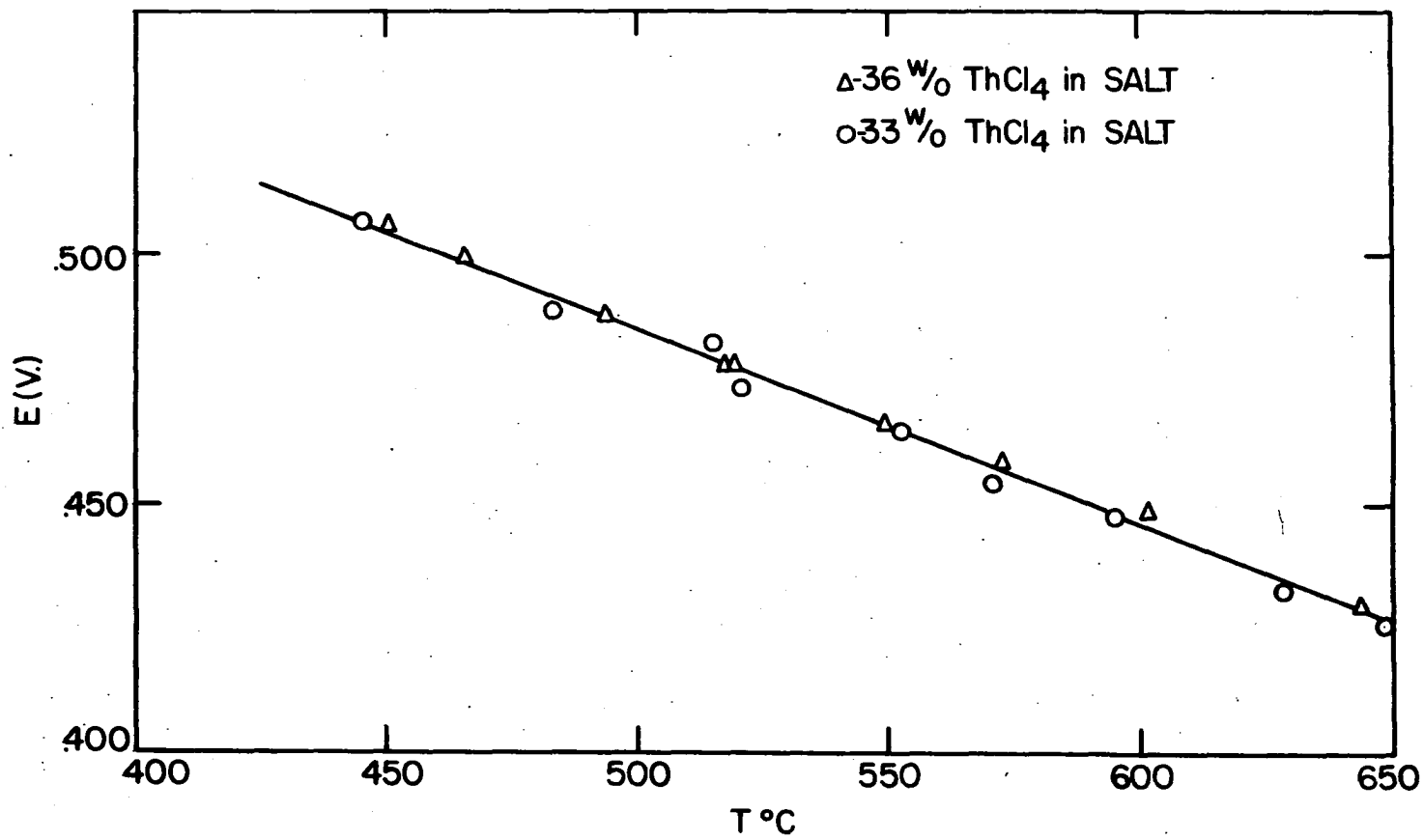
These results agree well with the values obtained by Chiotti

and Gill (13) using vapor pressure measurements. Their

results when fitted to a two constant equation can be ex-

pressed as

$$\Delta F^o_{Th_2Zn_{17}} = -145,000 + 72.1T \text{ calories/mole.} \qquad (48)$$

From this agreement, it would appear that at high concentra-

tions of thorium in the salt in equilibrium with the thorium-

zinc alloy, $ThCl_4$ is the predominant thorium chloride in solu-

tion. This observation is consistent with the predicted

effect discussed in the previous section, i.e., that as the

total thorium content in the salt becomes very high, the pre-

dominant species in solution should be $ThCl_4$.

CONCLUSIONS AND SUMMARY

The compounds $ThCl_3$ and $ThCl_2$ were prepared by reduction of $ThCl_4$ with thorium. To prepare $ThCl_3$, stoichiometric amounts of $ThCl_4$ and thorium for the reaction

$$3ThCl_4 + Th \rightarrow 4ThCl_3 \qquad (49)$$

were equilibrated at $800^{\circ}C$ for 26 hours, rapidly cooled, and equilibrated at $650^{\circ}C$ for 64 hours. The resulting product was purplish-black with very little unreacted thorium evident. This product was heated under vacuum at $500^{\circ}C$ for two hours to remove any unreacted $ThCl_4$. The residue analyzed 33.2 wt.% Cl and 63.3 wt.% Th, giving a chlorine to thorium ratio of 3.2 to 1. An x-ray powder pattern of this material showed some weak $ThCl_4$ lines plus many other lines concluded to be those of $ThCl_3$. These lines could not be indexed and probably represent a unit cell of orthorhombic or lower symmetry.

To prepare $ThCl_2$, stoichiometric amounts of $ThCl_4$ and thorium for the reaction

$$ThCl_4 + Th \rightarrow 2ThCl_2 \qquad (50)$$

were equilibrated at $800^{\circ}C$ for 26 hours, rapidly cooled, and equilibrated at $715^{\circ}C$ for 64 hours. Some unreacted thorium still remained indicating that the reaction had not gone to completion. A gray black material was found on the surface

of the remaining thorium metal. The chemical analyses of this material were 76.3 wt.% Th and 24.0 wt.% Cl, giving a chlorine to thorium ratio of 2.02 to 1. An x-ray analysis of this material gave a distinct but complex powder pattern which could not be accounted for by the powder patterns of $ThCl_4$ or the pattern of the trichloride described above. The conclusion is that this material is $ThCl_2$. These lines could not be indexed and also probably represent a unit cell of orthorhombic or lower symmetry.

The possibility of the existence of a polynuclear cage complex in this system similar to those of tantalum, $[Ta_6Cl_{12}]Cl_2$, discussed by Pauling (28) and recently investigated by McCarley and Hughes (31) was considered. No definite evidence for the existence of such a complex was found.

As a check that none of the lines in the x-ray powder patterns of the $ThCl_3$ and $ThCl_2$ were those of $ThOCl_2$, they were compared with a pattern of the oxychloride. Stoichiometric amounts of $ThCl_4$ and $ThOCl_2$ for the reaction

$$ThCl_4 + ThO_2 \rightarrow 2ThOCl_2 \tag{51}$$

were equilibrated at 800°C for 55 hours. The resulting $ThOCl_2$ was composed of white, fluffy, acicular crystals very much like the $ThOI_2$ described by Wylie (24). The x-ray

powder pattern of the $ThOCl_2$ showed a tremendous number of

lines, none of which matched those of the $ThCl_3$ or $ThCl_2$.

Thermal data obtained from equilibrated $Th-ThCl_4$ mixtures

are consistent with the existence of $ThCl_3$ and $ThCl_2$ and were

used in constructing a tentative phase diagram. The data

indicates that $ThCl_3$ disproportionates at $698^{\circ}C$ to $ThCl_4$ and

$ThCl_2$, and that $ThCl_2$ decomposes peritectically at $748^{\circ}C$.

The disproportionation of $ThCl_3$ may be represented by the

reaction

$$2ThCl_3 \rightarrow ThCl_2 + ThCl_4. \tag{52}$$

The data indicate negligible mutual solubility among these

compounds, and therefore the standard free energies of forma-

tion at $698^{\circ}C$ must satisfy the relation

$$2\Delta F^{O}_{ThCl_3} = \Delta F^{O}_{ThCl_2} + \Delta F^{O}_{ThCl_4}. \tag{53}$$

Glassner's (10) relations for the standard free energies

of formation for $ThCl_4$ and $ThCl_3$ were simplified to give the

relations

$$\Delta F^{O}_{ThCl_4} = -286,400 + 129.2T - 19.3TlogT \text{ cal/mole} \tag{54}$$

and $\Delta F^{O}_{ThCl_3} = -231,800 + 96.9T - 13.8TlogT$ cal/mole. $\tag{55}$

The entropy of formation for $ThCl_2$ at $298^{\circ}K$ was assumed to be

-36.1 calories/mole-degree and ΔC_p of $ThCl_2$ for the tempera-

ture range 298° to $1100^{\circ}K$ was assumed to have a mean value

of 4.0 calories/mole-degree. With these assumptions and relation 53, the following equation for the standard free energy of formation of $ThCl_2$ was derived:

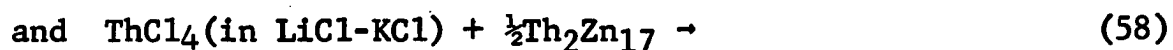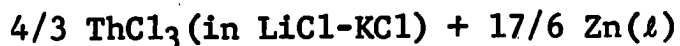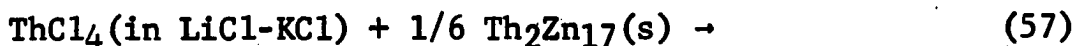$$\Delta F^o_{ThCl_2} = -172,900 + 62.9T - 9.2TlogT \text{ cal/mole.} \quad (56)$$

The electromotive force of the cell $Th/LiCl-KCl-ThCl_4//$ $LiCl-KCl-3.3$ wt.% $AgCl/Ag$ was measured for a concentration range of 0.1 to 32.4 wt.% $ThCl_4$ in the salt and a temperature range of 450-650°C. The data obtained from this cell indicate that the activity coefficient of $ThCl_4$ relative to the pure solid in LiCl-KCl is about 1×10^{-3} for these concentration and temperature ranges, and that this coefficient is rather insensitive to concentration and temperature, increasing only slightly with increased concentration and temperature.

The activity coefficients of $ThCl_3$ and UCl_3 should be about the same since the ionic radii of Th^{+3} and U^{+3} are very nearly equal (28). The activity coefficient of UCl_3 in the LiCl-KCl eutectic has been found to be very nearly unity (29, 30); therefore a value of one was assumed for the activity coefficient of $ThCl_3$ in this salt. Experimental data of equilibrations of $ThCl_4$ in LiCl-KCl with thorium metal indicate that $ThCl_2$ is relatively insoluble in the LiCl-KCl salt. These data indicate that the activity coefficient of $ThCl_2$

relative to the pure solid is about 1×10^3 at 700°C.

With the values of the activity coefficients of the thorium chlorides in LiCl-KCl discussed above and the free energy data for these thorium chlorides and the thorium-zinc compound, Th_2Zn_{17}, the expected extents of the reactions

$$ThCl_4(\text{in LiCl-KCl}) + 1/6\ Th_2Zn_{17}(s) \rightarrow \hspace{1cm} (57)$$

$$4/3\ ThCl_3(\text{in LiCl-KCl}) + 17/6\ Zn(l)$$

and $\ ThCl_4(\text{in LiCl-KCl}) + \tfrac{1}{2}Th_2Zn_{17} \rightarrow \hspace{1cm} (58)$

$$2ThCl_2(\text{in LiCl-KCl}) + 8.5Zn(l)$$

were calculated. Calculations show that reaction 57 should be the predominant reaction occurring in the LiCl-KCl-liquid zinc system since the very large activity coefficient of $ThCl_2$ and the very small activity coefficient of $ThCl_4$ in the salt inhibit reaction 58. Experimental results of equilibrations of solutions of $ThCl_4$ in the LiCl-KCl eutectic with Th_2Zn_{17} in zinc agree well with the predicted ratios of N_{ThCl_3}/N_{ThCl_4} in the salt. It was found that the relative amounts of $ThCl_3$ and $ThCl_4$ in the salt are dependent on the total thorium concentration in the salt and on temperature. Lower total thorium concentration in the salt and higher temperature are both found to favor higher N_{ThCl_3}/N_{ThCl_4} ratios in the salt, i.e., these factors both shift reaction 57 to the right. It

is concluded that in the LiCl-KCl-liquid zinc system, the predominant thorium chlorides in solution are $ThCl_4$ and $ThCl_3$, with the relative amounts of each depending on total thorium concentration in the salt and on temperature.

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ACKNOWLEDGMENTS

APPENDIX A

Derivation of Equations 34 and 35

Assume that the reaction

$$ThCl_4 + Th \rightarrow 2ThCl_2 \qquad (1a)$$

did not go to completion, but that the equilibrium

$$ThCl_4 + ThCl_2 \rightleftharpoons 2ThCl_3 \qquad (2a)$$

is attained, where $ThCl_2$ is an insoluble precipitate on the surface of the thorium metal.

At equilibrium, the total moles of thorium, n_T, is the sum of the moles of the tetra-, tri-, and dichlorides:

$$n_T = n_{ThCl_4} + n_{ThCl_3} + n_{ThCl_2}. \qquad (3a)$$

Dividing both sides of this equation by $\Sigma\, n$, the total moles of salt, gives this sum in terms of mole fractions:

$$N_{Th} = N_{ThCl_4} + N_{ThCl_3} + N_{ThCl_2}. \qquad (4a)$$

Let n_i be the initial moles of $ThCl_4$ added to the charge, $n_{Th,R}$ the moles of thorium which reacted, n_{2p} the moles of $ThCl_2$ that precipitated, and n_2, n_3, and n_4 the moles of di-, tri-, and tetrachloride in the salt at equilibrium. Then considering the reactions

$$ThCl_4 + 1/3\ Th \rightarrow 4/3\ ThCl_3 \qquad (5a)$$

and $\qquad ThCl_4 + Th \quad \rightarrow \quad 2ThCl_2, \qquad (6a)$
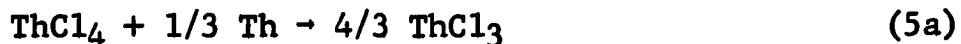
the following equation may be written:

$$n_i = n_4 + 3/4\ n_3 + 1/2\ n_2 + 1/2\ n_2 p. \qquad (7a)$$

But necessarily the number of moles of thorium as $ThCl_2$ that precipitated must be equal to the sum of the initial moles of thorium and the reacted moles of thorium minus the number of moles of thorium remaining in solution, i.e.,

$$n_2 p = n_i + n_{Th,R} - n_T. \qquad (8a)$$

Substituting this Equation 8a into Equation 7a, dividing by $\xi\ n$, and rearranging gives the following equation:

$$\tfrac{1}{2}N_i - \tfrac{1}{2}N_{Th,R} + \tfrac{1}{2}N_{Th} = N_{ThCl_4} + 3/4\ N_{ThCl_3} + \tfrac{1}{2}N_{ThCl_2}, \qquad (9a)$$

where the subscripts have the same meanings as before, but the equation is now in terms of mole fractions instead of numbers of moles. Multiplying Equation 9a by 2 and subtracting Equation 4a gives the following equation:

$$N_i - N_{Th,R} = N_{ThCl_4} + \tfrac{1}{2}N_{ThCl_3}. \qquad (10a)$$

But we have assumed that the equilibrium of reaction 2a has been established and also that the activity of $ThCl_2$ is unity. Therefore the equilibrium constant of reaction 2a may be written

$$K = \frac{N_{ThCl_3}^2\ \gamma_{ThCl_3}^2}{N_{ThCl_4}\gamma_{ThCl_4}a_{ThCl_2}} = \frac{N_{ThCl_3}^2\ \gamma_{ThCl_3}^2}{N_{ThCl_4}\ \gamma_{ThCl_4}}. \qquad (11a)$$

At $700^\circ C$, $K = 1$, $\gamma_{ThCl_3} = 1$, and $\gamma_{ThCl_4} = 1 \times 10^{-3}$. Substi-

tuting these values into Equation 11a gives the relationship:

$$N_{ThCl_3} = \sqrt{10^{-3}N_{ThCl_4}} \; . \tag{12a}$$

Substituting this expression into Equation 10a gives

$$N_i - N_{Th,R} = N_{ThCl_4} + \tfrac{1}{2}\sqrt{10^{-3}N_{ThCl_4}} \; . \tag{13a}$$

This is Equation 34 in the text.

If Equation 9a is multiplied by 4/3 and then Equation 4a is subtracted from it, the following equation is obtained for N_{ThCl_2}:

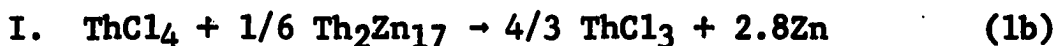$$N_{ThCl_2} = N_{ThCl_4} - 2N_i + 2N_{Th,R} + N_{Th} \; . \tag{14a}$$

This is Equation 35 in the text.

APPENDIX B

Derivation of Equation 41

The two reactions being considered are

$$\text{I.} \quad \text{ThCl}_4 + 1/6 \ \text{Th}_2\text{Zn}_{17} \rightarrow 4/3 \ \text{ThCl}_3 + 2.8\text{Zn} \tag{1b}$$

$$\text{and} \quad \text{II.} \ \text{ThCl}_4 + \tfrac{1}{2}\text{Th}_2\text{Zn}_{17} \rightarrow 2\text{ThCl}_2 + 8.5\text{Zn} \tag{2b}$$

The equilibrium constants for these two reactions may be written

$$K_I = K_{\gamma I} \ \frac{n_{\text{ThCl}_3}^{4/3}}{n_{\text{ThCl}_4}} \ \frac{1}{(\text{\large$\lessgtr$} n)^{1/3}} \tag{3b}$$

and

$$K_{II} = K_{\gamma II} \ \frac{n_{\text{ThCl}_2}^{2}}{n_{\text{ThCl}_4}} \ \frac{1}{\text{\large$\lessgtr$} n} \ , \tag{4b}$$

where n denotes number of moles and $\lessgtr n$ represents the total moles of salt phase.

Equation 3b may be solved for n_{ThCl_3} in terms of n_{ThCl_4}:

$$n_{\text{ThCl}_3} = \left(\frac{K_I}{K_{\gamma I}}\right)^{3/4} n_{\text{ThCl}_4}^{3/4} (\text{\large$\lessgtr$} n)^{1/4}. \tag{5b}$$

Likewise Equation 4b may be solved for n_{ThCl_2} in terms of n_{ThCl_4}:

$$n_{\text{ThCl}_2} = \left(\frac{K_{II}}{K_{\gamma II}}\right)^{\tfrac{1}{2}} n_{\text{ThCl}_4}^{\tfrac{1}{2}} (\text{\large$\lessgtr$} n)^{\tfrac{1}{2}} \tag{6b}$$

But the total number of moles of thorium in the salt, n_{Th}, is equal to:

$$n_{\text{Th}} = n_{\text{ThCl}_4} + n_{\text{ThCl}_3} + n_{\text{ThCl}_2}. \tag{7b}$$

Substituting Equations 5b and 6b into Equation 7b gives:

$$n_{Th} = n_{ThCl_4} + \left(\frac{K_I}{K_{\gamma I}}\right)^{3/4} n_{ThCl_4}{}^{3/4} (\Sigma n)^{1/4} +$$

$$\left(\frac{K_{II}}{K_{\gamma II}}\right)^{\frac{1}{2}} n_{ThCl_4}{}^{\frac{1}{2}} (\Sigma n)^{\frac{1}{2}}. \qquad (8b)$$

Finally, dividing Equation 8b through by Σn, the total number

of moles, gives:

$$N_{Th} = N_{ThCl_4} + \frac{K_I}{K_{\gamma I}}{}^{3/4} N_{ThCl_4}{}^{3/4} + \frac{K_{II}}{K_{\gamma II}}{}^{\frac{1}{2}} N_{ThCl_4}{}^{\frac{1}{2}}.$$

$$(9b)$$

This is Equation 26 in the text.