

the long range of temperature extrapolation, the experimental value is expected to be lower than the extrapolated one in view of the temperature dependence of the Sutherland "constant" over a wide range of temperatures (1).

The molecular diameters, σ , shown in the last column of Table I were calculated from the viscosity data using the smooth hard elastic sphere model (1). For methanol and ethanol, the coefficients of viscosity from Titani were used and the others from the values determined in this work. The expected trends of increasing diameter with increasing chain length, and the systematic reduction due to chain branching are seen to be in evidence.

LITERATURE CITED

- (1) Chapman, S., Cowling, T.G., "The Mathematical Theory of Non-Uniform Gases," 2nd ed., Cambridge University Press, London, 1952.
- (2) Johnston, H.L., McCloskey, K.E., *J. Phys. Chem.* **44**, 1093 (1939).
- (3) Nemeth, E.M., Ph. D. dissertation, Loyola University, Chicago, 1963.
- (4) Titani, T., *Bull. Chem. Soc. Japan* **8**, 255 (1933).

RECEIVED for review December 12, 1963. Accepted April 6, 1964. Abstracted in part from the Ph. D. thesis of E.M. Nemeth, Loyola University, (1963).

Distribution Coefficients for Certain Actinide and Fission Product Chlorides in the Immiscible Salt System: LiCl-KAlCl₄

R. H. MOORE

General Electric Co., Richland, Wash.

Two nearly immiscible molten salt phases, KAlCl₄ and LiCl, are obtained in the ternary system: LiCl-KCl-AlCl₃. Metal chlorides and oxychlorides dissolve in and distribute between these two solvent phases in practical amounts. The distribution data show that potentially useful separations can be achieved by partitioning solutes between these phases. The distribution coefficients range from 18.1 for Cs⁺ to 0.014 for Sr²⁺.

THE TERNARY SALT SYSTEM, LiCl-KCl-AlCl₃, exists as two immiscible phases over an appreciable composition and temperature range (2). Compositions which yield two liquid phases can be obtained from 350° to 775° C. Below 350°, solid separation commences in one or both phases. Above 775°, the consolute temperature, only a single liquid phase exists.

The principal constituent of the phase of lower density is the complex, KAlCl₄. The phase of higher density is mainly LiCl. The phases have a small mutual solubility.

Metal chlorides and oxychlorides dissolve and distribute in the partly immiscible phases. Large quantities of solute coalesce the phases, but this does not occur until as much as 25 to 30 weight per cent of solute has been added.

The immiscible phases are highly mobile liquids, about as fluid as water. They disperse and disengage with ease. Molten salts are resistant to radiation damage, and this system may find application in separations processing of intensely radioactive materials. With this in mind, attention was focused on determination of the distribution coefficients of a number of fission product and actinide element chlorides and oxychlorides. From these data the separations capability of a practical process can be deduced.

The immiscible phases constitute pairs of conjugate ternary solutions with variable composition. Figure 1 is an isothermal section through the isobaric prism. Compositions indicated by asterisks on each tie line yield immiscible phases of composition indicated by open circles at the points of intersection of the tie lines and the binodal curve. The compositions indicated by solid circles and connected by a heavy dashed line are typical of the compositions used in this work. These compositions provided an excess

of chloride ion over that needed to complex AlCl₃. This leads to a solvent less susceptible to hydrolysis by atmospheric moisture and reduces competition between AlCl₃ and added solute for available chloride ion. Such competition could have a marked effect on the composition of the distributing solute.

EXPERIMENTAL

A weighed quantity of anhydrous solute was added to a known quantity of premelted immiscible phases. The solvent phases contained in an open 200 mm. × 25 mm. Vycor test tube were heated by a Lindbergh Model Cr-15 Pot Furnace. Addition of the solute would normally disturb the temperature equilibrium; while temperature equilibrium was being reestablished, the system was stirred to disperse the phases and assist dissolution of the solute. Stirring was done manually with a quartz thermocouple protection tube enclosing a chromel-alumel thermocouple connected through a bucking variable potentiometer to a 0-2 mv. scale recorder. With this arrangement temperatures could be measured to ±0.5° at 625° C.

When temperature equilibrium was reestablished, stirring was stopped to permit the phases to disengage. Approximately 2.0 ml. was then withdrawn from each 25 ml. phase with pipettes preheated to the equilibration temperature. The molten samples were quenched by pouring them onto a stainless steel plate, after which they were weighed, dissolved in 3M HCl, and analyzed for the distributing cation and solvent metal ions. The large conversion factors needed to convert these data to weight per cent metal chloride multiplies small analytical errors. The

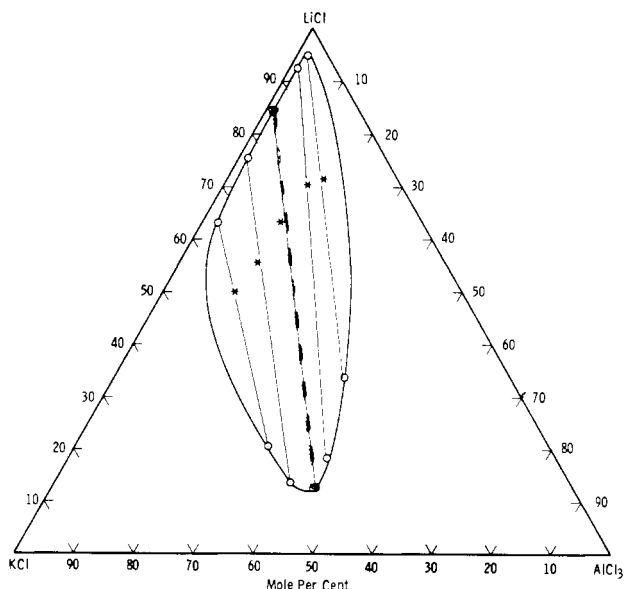
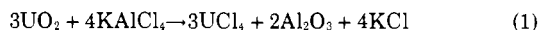


Figure 1. Isobaric section at 625° C. through the isobaric prism system: LiCl-KCl-AlCl₃

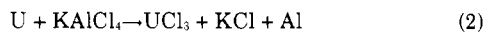
results indicate, however, that the cation analyses were generally accurate to within one per cent.

Methods for preparing the anhydrous solvent salts have been described (2). Anhydrous UO₂Cl₂, CeCl₃, FeCl₃, SrCl₂, and RuCl₃ were prepared by careful heating in a stream of anhydrous HCl. PuCl₃ was prepared from PuO₂ by reaction with phosgene at 400° C. UCl₄ was prepared in situ in the KAlCl₄ phase by reaction with UO₂:



The Al₂O₃ was allowed to settle to the bottom of the Vycor tube, after which the salt was frozen. Upon removal of the tube, the end of the salt containing the Al₂O₃ was cropped and discarded.

UCl₃ was also prepared in situ by reaction of KAlCl₄, in this case, with uranium metal:



No attempt was made to remove traces of aluminum formed in this reaction.

DATA AND DISCUSSION

Data in Figure 2, 3, and 4 were obtained with UO₂Cl₂, CsCl, and RuCl₃ as the distributing solutes. These data are typical of variable solute concentration. The distribu-

tion coefficient is obtained from the slope of these curves and is expressed as the mole fraction of solute in the KAlCl₄ phase (top phase) divided by the mole fraction of solute in the LiCl phase (bottom phase). Figures 2, 3, and 4 show that UO₂Cl₂ and RuCl₃ concentrate in the LiCl phase while CsCl favors the KAlCl₄ phase.

It is tempting to conclude, from the linearity of these plots, that the distribution law is obeyed. Unfortunately, the solvents change composition due to their increased mutual solubility as solute is added. It is therefore not possible to state that the distribution law is obeyed, although, for practical purposes, these data can be treated as though this were the case.

With regard to possible species present, pure anhydrous UO₂Cl₂ is reported to be unstable above 500° C., but forms stable double salts of the composition K₂UO₂Cl₄ (1). In systems of high chloride ion activity, such as these, it is probable that the complex anion, UO₂Cl₄⁻², is the distributing species.

By analogy with its aqueous chemistry, RuCl₃ would also be expected to form complex chloro anions. Its solutions in these salt phases exhibit intense reddish brown color similar to that in aqueous 12M HCl solutions at high ruthenium concentrations. It is probable the distributing species is the anion, RuCl₆⁻³.

The distribution coefficient of 18.1 for CsCl is the largest observed for any substance so far tested. Continued addition of CsCl beyond the concentration limits of Figure 4 results in phase inversion. Analysis reveals that K⁺ has been displaced from its complex with AlCl₃. Here the Cs⁺ ion is the distributing species.

UO₂Cl₂ is quite stable to air oxidation or hydrolysis; UCl₄ is rapidly oxidized to UO₂Cl₂ and must be protected from oxidation. SnCl₂ rapidly reduces UO₂Cl₂ to form UO₂ and SnCl₄. UO₂ is then redissolved as by Reaction 1. Thus, SnCl₂ proves to be a useful holding reductant to prevent oxidation of UCl₄ to UO₂Cl₂.

Data in Table I illustrate the effectiveness of SnCl₂ in this respect. With the container open to air, samples taken at intervals during 160 minutes show no significant changes in the distribution coefficient for UCl₄. The concentration of SnCl₂ gradually decreased as it was oxidized to volatile SnCl₄ and escaped. These data also permitted calculation of the distribution coefficient for SnCl₂.

Spectrophotometric measurements by Morrey (3) on molten solutions of UCl₄ in KAlCl₄ and various alkali halide solvents have established that the uranium species present is predominately UCl₆⁻². The spectrophotometric measurements indicated further that the UCl₆⁻² species is more stable in CsAlCl₄ or KAlCl₄ than in CsCl, KCl, or NaCl.

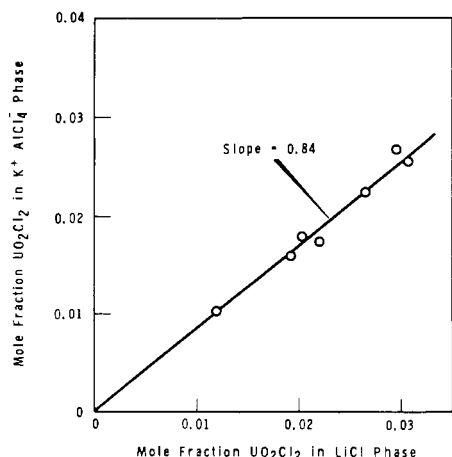


Figure 2. Distribution of UO₂Cl₂ at 625° C.

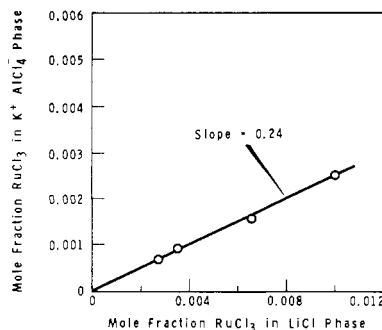


Figure 3. Distribution of RuCl₃ at 625° C.

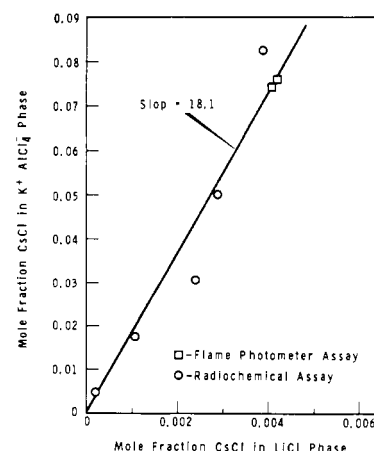


Figure 4. Distribution of CsCl at 625° C.

Table I. Distribution of UCl_4 (and $SnCl_2$) at $625^\circ C$.^a

Sample Time	w/o		w/o		w/o		D^b , UCl_4 Basis	K_D^b , UCl_4 Mole Fraction Basis	D^b , $SnCl_2$ Basis	K_D^b , $SnCl_2$ Mole Fraction Basis
	LiCl	KCl	$AlCl_3$	UCl_4	$SnCl_2$					
15 ^c	17.3	25.9	53.6	2.98	2.57	1.0	1.70	0.4	0.7	
	77.0	9.3	5.9	2.98	6.21					
33 ^c	18.8	24.3	53.1	2.70	2.56	0.95	1.62	0.5	0.9	
	76.7	9.4	6.5	2.84	5.13					
83 ^c	13.8	29.1	56.5	2.70	...	0.85	1.48	
	76.6	9.6	5.6	3.19	4.30					
160 ^c	14.7	26.1	55.4	2.79	0.27	0.91	1.69	0.5	0.9	
	79.7	11.3	5.0	3.08	0.56					

^aUnder the w/o columns two values are given. The uppermost is the composition of the $KAlCl_4$ phase and the lower is the composition of the LiCl phase.

$$^b D = \frac{\text{w/o U in } KAlCl_4}{\text{w/o U in LiCl}}$$

$$K_D = \frac{\text{Mole Fraction U in } KAlCl_4}{\text{Mole Fraction U in LiCl}}$$

^cTime in minutes from the time at which the phases attained the equilibration temperature until samples were taken.

Table II. Distribution of UCl_3 at $625^\circ C$.^a

w/o LiCl	w/o KCl	w/o $AlCl_3$	w/o UCl_3	D^b w/o Basis	K_D^b Mole Fraction Basis
87.1	8.0	5.0	4.69	0.017	0.027
10.1	38.3	60.8	0.12		
87.6	10.8	3.1	7.15	0.030	0.056
10.1	28.8	60.9	0.18		
81.7	12.0	5.4	6.09		

^aSee footnote a, Table I. ^bSee footnote b, Table I.

UCl_3 for which data are shown in Table II was produced in situ in accordance with Reaction 2. This reaction proceeded to completion in from 45–60 seconds after which molten LiCl was added in predetermined amount. Samples were taken as quickly as possible after temperature equilibrium was attained. In all cases extraction of UCl_3 into the LiCl phase appeared complete, leaving a water white $KAlCl_4$ phase. Analysis later showed detectable amounts of uranium in this phase—amounts which would surely have been visible if present as intensely colored UCl_6^{-3} ions. The amount of uranium could have gone unnoticed if present as the less intensely colored $UO_2Cl_4^{-2}$ which would be the stable end product of UCl_3 oxidation. In any case it is interesting that the distribution coefficient for UCl_3 is so much smaller than that for UO_2Cl_2 or UCl_4 . Clearly, uranium can be transferred from one phase to the other simply by altering its oxidation state.

It has been assumed that in these systems, the chloride ion activity is high enough to ensure formation of the complex chloro anions. If so, the behavior of UCl_6^{-3} is anomalous, for in all other cases, the complex anion has been shown to favor the $KAlCl_4$ phase. Uncomplexed UCl_3 exhibits extremely low solubility in stoichiometric $KAlCl_4$ (4) which would lead to the expectation that uncomplexed UCl_3 would favor the LiCl phase in this two phase system. It therefore appears that in the presence of large concentrations of $AlCl_3$ and Li^+ which compete for the chloride ion, that the chloride ion activity was not high enough to ensure formation of UCl_6^{-3} and that the distributing species was actually UCl_3 .

The behavior of $PuCl_3$ and $PuCl_4$ parallels that of UCl_3 and UCl_4 . $PuCl_4$ can be produced in solution from $PuCl_3$ by reaction with chlorine. When chlorine is bubbled through the melt, the agitation produced is sufficient to disperse the phases. Dissolved chlorine will continue to

hold plutonium in the IV state for an appreciable period after the chlorine sparge is withdrawn. Under these conditions, a distribution coefficient of 1.90 is obtained.

With $SnCl_2$ simultaneously present, the relatively unstable $PuCl_4$ reduces to $PuCl_3$ (difference from UCl_4). Under these conditions a distribution coefficient of 0.040 results.

Advantage can be taken of the variable stability of UCl_4 and $PuCl_4$ to effect their separation. Earlier it was shown that UCl_4 is stable in the presence of $SnCl_2$. $PuCl_4$, however, reduces to $PuCl_3$. In the presence of $SnCl_2$, therefore, it is possible to obtain UCl_4 and $PuCl_3$ in the same solution. Their distribution coefficients differ by a factor of 40 with UCl_4 favoring the $KAlCl_4$ phase and $PuCl_3$ favoring the LiCl phase.

Ferric and ferrous chlorides are also useful reagents for control of the oxidation state of distributing solute species. Ferric chloride exhibits a distribution coefficient of 9.1. The magnitude of this distribution coefficient indicates that $FeCl_3$ resembles $AlCl_3$ in its tendency to form anionic complexes, e.g., $FeCl_4^{-1}$. In separate experiments, it was demonstrated that the compound $KFeCl_4$ also exhibits immiscibility with LiCl.

Ferric chloride oxidizes UCl_3 to UCl_4 as evidenced by the progressive increase in uranium halide distribution coefficients upon addition of ferric chloride. So long as any UCl_3 remains, the iron species present is obviously the ferrous ion and its distribution coefficient is 0.75.

The distribution behavior of cerium chloride is illustrated in Figure 5. Cerium was introduced as $CeCl_3$ traced with Ce^{144} . In the presence of $SnCl_2$, a distribution of 8.6×10^{-2} was obtained. The experiment was then repeated with chlorine bubbled through the solvent salts and no addition of $SnCl_2$. Under these conditions a distribution of 2.7×10^{-2} was obtained. After additional $CeCl_3$ was added, the system

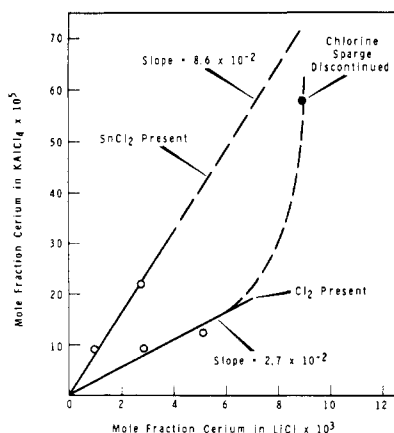


Figure 5. Distribution of cerium chloride at 625°C.

was allowed to stand for 40 minutes with no chlorine sparge, and then samples were taken which yield the point shown as a solid circle and a distribution calculated to be 5.9×10^{-2} .

With SnCl_2 present, the distribution coefficient should be that due to CeCl_3 , probably the CeCl_6^{-3} complex anion. With chlorine present, oxidation to CeCl_4 would be anticipated, and since this is an unstable substance at a temperature of 625°C, removal of the chlorine sparge should result in reversion to CeCl_3 , as appeared to occur.

The CeCl_6^{-3} complex ion is a larger anion than the CeCl_6^{-2} complex ion and it exhibits a larger distribution coefficient as was expected for the trivalent complexes of uranium and plutonium. Evidently the CeCl_6^{-3} complex ion is appreciably more stable than UCl_6^{-3} or PuCl_6^{-3} and is formed at the chloride ion activity which prevails in this system.

The distribution data are summarized in Table III. In general, these data were obtained with the distributing species as the sole solute unless oxidizing or reducing

Table III. Distribution Coefficients for Metal Chlorides in the System: LiCl-KAlCl_4 at 625°C.

Probable Species		K_D
Distributing		
UO_2Cl_2	$\text{UO}_2\text{Cl}_4^{-2}$	0.84
$\text{UCl}_4(+\text{SnCl}_2)$	UCl_6^{-2}	1.62
UCl_3	UCl_3	0.04
$\text{PuCl}_4(+\text{Cl}_2)$	PuCl_6^{-2}	1.9
PuCl_3	PuCl_3	0.04
$\text{CeCl}_3(+\text{Cl}_2)$	CeCl_6^{-2}	0.03
$\text{CeCl}_3(+\text{SnCl}_2)$	CeCl_6^{-3}	0.09
$\text{FeCl}_2(+\text{UCl}_3, \text{excess})$	FeCl_4^{-2}	0.75
FeCl_3	FeCl_4^{-1}	9.1
RuCl_3	RuCl_6^{-3}	0.24
SnCl_2	SnCl_4^{-2}	0.9
SrCl_2	Sr^{+2}	0.014
NaCl	Na^-	0.56
CsCl	Cs^+	18.1

agent was required, as indicated. There is no evidence that these data will hold for a given distributing solute in more complex mixtures. Consequently, the data are merely indicative of the results to be anticipated in a practical case. However, the data indicate that a number of separations of practical interest can be achieved.

LITERATURE CITED

- (1) Katz, J.J., Rabinowitch, E., "The Chemistry of Uranium, Part I. The Element, Its Binary and Related Compounds," p. 583, McGraw-Hill, New York, 1951.
- (2) Moore, R.H., J. CHEM. ENG. DATA 8, 164, (1963).
- (3) Morrey, J.R., *Inorg. Chem.* 2, 163 (1963).
- (4) Morrey, J.R., Private communication, General Electric Co., Richland, Wash., August 8, 1962.

RECEIVED for review December 16, 1963. Accepted April 16, 1964. Work performed under contract AT(45-1)-1350 for the U. S. Atomic Energy Commission.

High-Temperature Heat Content of Niobium

DONALD T. HAWKINS and RAYMOND L. ORR

Lawrence Radiation Laboratory and Department of Mineral Technology, University of California, Berkeley, Calif.

High-temperature heat contents of niobium were measured over the temperature range 298° to 1415° K., using a diphenyl ether calorimeter. Smoothed values of the thermal properties of niobium, $H_f^\circ - H_{298}^\circ$, C_p , $S_f^\circ - S_{298}^\circ$, and $(F_f^\circ - H_{298}^\circ)/T$, have been derived and are tabulated at even 100° intervals. Within an average deviation of 0.10%, the tabular heat content values are given by the expression:

$$H_f^\circ - H_{298,15}^\circ = 5.885T + 4.044 \times 10^{-4}T^2 + 2.194 \times 10^4T^{-1} - 1864.$$

GROWING INTEREST IN NIOBIUM as a high-temperature refractory metal plus the availability of a sample of high purity material have made it desirable to determine the high-temperature thermal properties of niobium by means of heat content measurements. Previously reported measurements of the high-temperature thermal properties of niobium by Jaeger and Veenstra (5) ($H_f^\circ - H_{295}^\circ$, 670° - 1828° K.), Lowenthal (9) (C_p , 1471° - 2259° K.), and Gel'd and Kusenko (2) ($H_f^\circ - H_{298}^\circ$, 433° - 1840° K.) are not in agreement. The data of the latter investigators, while recent and extensive, were reported for niobium containing 1.0% oxygen and 0.05%

carbon. This paper reports the results of heat content measurements on pure niobium in the temperature range 298° to 1415° K.

EXPERIMENTAL

Electron-beam melted niobium supplied by the Temescal Metallurgical Corp. was used in the study. The stated maximum impurity levels indicate the sample to have a purity of 99.99+% Nb.

Heat content measurements were made using a diphenyl ether Bunsen-type drop calorimeter. The apparatus and