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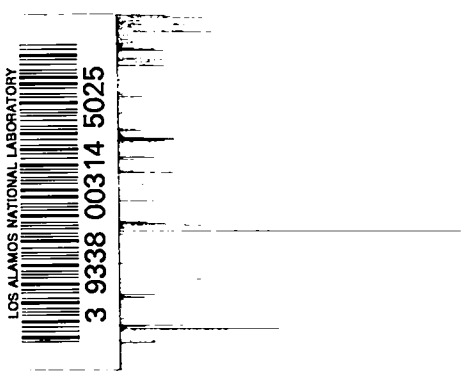

UNITED STATES
ATOMIC ENERGY COMMISSION
CONTRACT W-7405-ENG. 36

LA-3562
UC-4, CHEMISTRY
TID-4500

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Report written: May 17, 1966

Report distributed: December 1, 1966

Distribution of Americium Between Liquid Plutonium and a Fused Salt. Evidence for Divalent Americium

by

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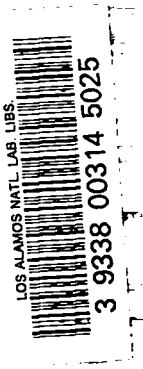

ABSTRACT

The distribution of Am between liquid Pu metal and a fused salt of NaCl-KCl containing $PuCl_3$ has been studied at 698, 730, and 775°C. over a $PuCl_3$ mole fraction range of 6×10^{-3} to 2×10^{-2}. The distribution data are consistent with the following equation

$$\underset{\text{metal phase}}{Am\ (\ell)} + \underset{\text{salt phase}}{\frac{2}{3}\ PuCl_3\ (\ell)} = \underset{\text{metal phase}}{\frac{2}{3}\ Pu\ (\ell)} + \underset{\text{salt phase}}{AmCl_2\ (\ell)}.$$

From the temperature dependence of the equilibrium constant, a value of -3.5 kcal. was obtained for ΔH^o for the above reaction.

ACKNOWLEDGMENTS

The authors are indebted to R. L. Nance for the $PuCl_3$, to K. W. R. Johnson for the Am, to Group CMB-1 for radiochemical analyses, and to G. M. Campbell who assisted with the computer programming.

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INTRODUCTION

Americium-241 grows into Pu at the rate of about 15 p.p.m. per month as the result of β decay of Pu-241. The chemistry of trace amounts of Am in molten Pu-molten salt systems has been discussed in earlier publications.[1, 2] When $PuCl_3$ is equilibrated at high temperature with Am dissolved in liquid Pu, the Am is preferentially oxidized and concentrates in the molten salt phase.

This report summarizes the results of a study of the heterogeneous equilibrium between Am and Pu in liquid metal-molten salt systems.

EXPERIMENTAL

Equipment

The equipment used for the distribution studies is shown in Fig. 1. The salt and metal phases were contained in a Ta crucible and were mixed by a motor driven Ta stirrer. The crucible was positioned in a stainless steel furnace tube which was heated by a Hevi-Duty Electric Co. tube furnace, Model M-5012. The upper furnace tube head contained seals and fittings for a stirrer, six sampling tubes, two Ta tubes which served as thermocouple sheaths, a gas-vacuum line, and a motor support rod. The bottom furnace tube cover contained a fitting for an Ar line. Temperatures were measured with a chromel alumel thermocouple immersed in the liquid metal phase and were recorded with a Brown Honeywell recorder. The thermocouple was protected by a Ta sheath. The temperature was controlled by a Wheelco Potentiotrol which was activated by a thermocouple positioned in the

thermocouple well shown in Fig. 1. The atmosphere in the furnace tube was Ar which was purified by passing welding grade Ar (99.998% purity) through a U chip furnace at 700°C.

Procedure

Approximately 700 g. of metal and 280 g. of salt were placed in the Ta cup shown in Fig. 1 and heated to melting. The sampling tubes were positioned 1 in. above the molten salt phase to minimize temperature changes during the sampling process, and the stirrer and thermocouple were lowered into the melt. The controller was set at the desired temperature, and the stirrer was activated. After at least 1 hr. at a constant temperature (± 0.5°C.), the stirrer was stopped, and the salt and metal phases were sampled. The metal sample was taken by simply lowering the Ta sampling tube into the metal phase. The salt phase was sampled by lowering an evacuated Ni filter tube into the salt phase and filtering the salt through the Ni frit by pressurizing the furnace to ~3 p.s.i.g. Samples of both phases were taken at the same time. The sample tubes were permitted to fill for approximately 3 min. The recorded temperature dropped as much as 4°C. during this 3-min. period. All temperatures listed in the tables are the equilibration temperatures. The tubes were then raised into the cold zone of the furnace tube which resulted in freezing the salt and metal samples. The furnace was then set at a higher or lower temperature or in some cases kept at the same temperature. After temperature equilibrium was again established the mixing of both phases was continued for at least 1 hr. and the sampling process repeated. After three salt and three metal samples had been taken in this manner the furnace was cooled to 480°C. to freeze the metal and salt, and the furnace tube head was replaced with a blank flange. An Ar atmosphere was maintained in the furnace at all times.

The metal samples were removed from the Ta tubes and were pickled in 4M HNO_3 to remove any adherent salt prior to dissolution in 6M HCl. The

(1) Metal phase
(2) Salt phase
(3) Ta crucible, 2-1/2 in. O.D., 2-7/16 in. I.D., 3-1/4 in. tall
(4) Ni crucible, 2-13/16 in. O.D., 2-11/16 in. I.D., 9-1/2 in. tall
(5) Thermocouple well, 1/2 in. diam. x 2 in. deep
(6) Ta stirrer, 1/4 in. O.D. rod, 16 in. long, 3/4 in. diam. impellers spaced 1-1/4 in. apart
(7) Ni adapter, 9/16 in. wide, 3/4 in. long, 1/2 in. tall
(8) Ni rod, 1/4 in. O.D., 10 in. tall
(9) Ni filter tube for salt phase samples, 5/16 in. O.D., 1-1/2 in. tall, 5/16 in. I.D., 1-1/4 in. deep; frit dimensions 5/16 in. O.D., 1/16 in. thick
(10) Ta rod, 1/8 in. diam., 2-1/2 in. tall
(11) Ni rod, 1/4 in. diam., 10 in. long
(12) Ta adapter tube, 3/8 in. O.D., 1/4 in. I.D., 3 in. tall; milled slot 3/16 in. wide, 2 in. tall
(13) Ta sampling tube for metal phase, 1/4 in. O.D., 1-1/2 in. long; two milled slots 1/8 in. wide, 1/2 in. tall
(14) Stainless steel furnace tube, 5 in. O.D., 4-3/4 in. I.D., 20 in. long
(15) Stainless steel pedestal, 9 in. tall
(16) Stainless steel spacer, 4-1/2 in. O.D., 2-7/8 in. I.D., 3-1/2 in. tall
(17) Ar inlet port

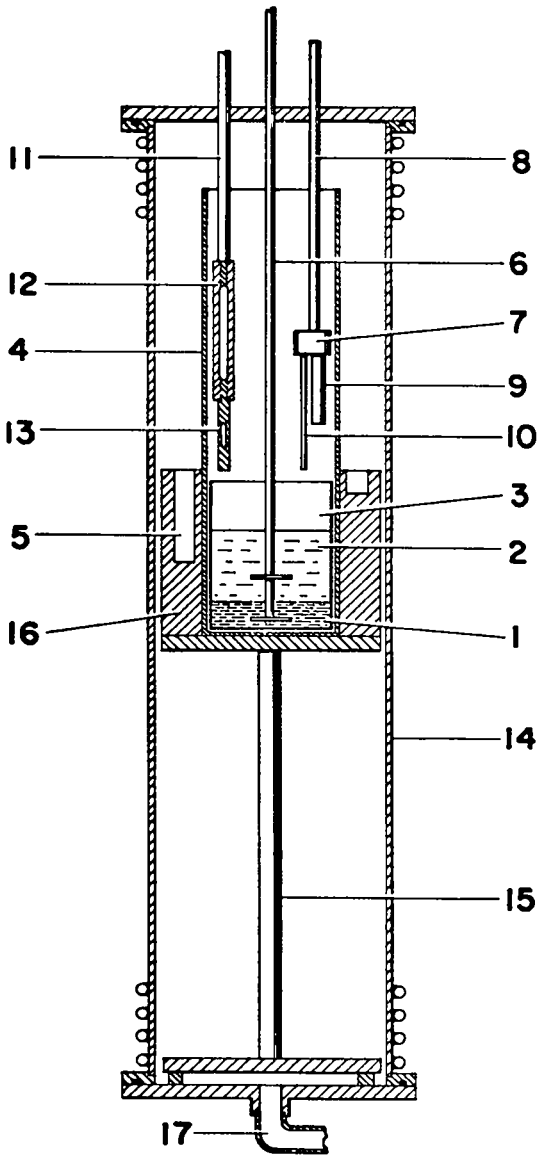

Fig. 1. Equipment for Distribution Studies

salt samples were removed as quantitatively as possible from the Ni tubes and were dissolved in 4M HNO_3. Plutonium and Am were determined radiochemically.[3]

To conduct an experiment at a different temperature or at a different $PuCl_3$ or $AmCl_3$ concentration the blank flange was removed from the furnace, the desired amount of salt or metal was added, and the sampling tube head was installed. The results were shown to be reversible with respect to direction of approach of temperature and Pu and Am concentrations (i.e., the same results were obtained when Am was transferred from salt to metal phase or when Am was transferred from metal to salt phase). Equilibrium was achieved in less than 1 hr. at a constant temperature.

Preparation of Materials

NaCl-KCl... An equimolar mixture of the salts was prepared by melting Baker's A.R. grade salts under vacuum.

$PuCl_3$... The $PuCl_3$ was prepared by the hydrochlorination of $Pu_2(C_2O_4)_3$, followed by vacuum distillation of the $PuCl_3$.

Pu... The Pu was electrorefined grade metal.

Am... The Am metal was obtained by the reduction of Am_2O_3 with La and distillation of the Am.[4]

RESULTS AND DISCUSSION

The results of the distribution experiments at 698, 730, and 775°C. are given in Tables 1, 2, and 3.

The extraction of Am from the metal into the salt phase can be represented by the generalized equation

$$\underset{\text{(Pu phase, } N_{Am})}{Am\ (\ell)} + \underset{\text{(salt phase, } N_{PuCl_x})}{\frac{y}{x} PuCl_x\ (\ell)} = \underset{\text{(salt phase, } N_{AmCl_y})}{AmCl_y\ (\ell)} + \underset{\text{(Pu phase, } N_{Pu})}{\frac{y}{x} Pu\ (\ell)}. \quad (1)$$

Table 1

Distribution of Am and Pu at 698°C.

Salt Phase - Equimolar NaCl-KCl Containing Pu and Am

Pu in Salt, wt. %	Am in Salt, wt. % x 10^2	Am in Metal, wt. % x 10^3
2.14	6.76	8.32
2.20	6.96	7.87
2.29	6.89	7.56
2.61	7.71	6.92
3.04	7.15	6.08
5.44	8.33	4.89
5.62	7.49	4.31
6.08	8.14	4.42
6.76	8.48	4.39
9.78	7.58	3.38
11.20	8.15	2.99

Table 2

Distribution of Am and Pu at 730°C.

Salt Phase - Equimolar NaCl-KCl Containing Pu and Am

Pu in Salt, wt. %	Am in Salt, wt. % x 10^2	Am in Metal, wt. % x 10^3
2.30	6.70	7.23
2.40	6.95	7.57
2.66	7.54	7.43
2.67	7.34	7.36
2.90	7.84	7.37
3.51	8.04	6.81
3.55	7.99	6.84
3.72	8.26	6.35
4.78	12.0	8.41
5.52	8.28	4.84
5.66	7.58	4.83
5.88	8.06	4.86
6.06	7.99	4.83
7.01	6.78	3.72
7.80	8.64	4.40
8.13	7.58	3.96
8.22	8.88	4.71

Table 3

Distribution of Am and Pu at 775°C.

Salt Phase - Equimolar NaCl-KCl Containing Pu and Am

Pu in Salt, wt. %	Am in Salt, wt. % x 10^2	Am in Metal, wt. % x 10^3
2.15	6.53	8.34
2.28	6.57	8.17
2.51	7.20	7.42
2.56	6.83	7.44
2.58	6.85	7.34
3.76	10.7	9.05
3.88	10.2	9.01
4.56	11.7	9.38
5.27	8.00	5.40
5.78	7.11	4.68
5.89	5.02	3.73
5.98	7.29	4.70
7.81	7.36	3.89
8.56	6.96	3.82

The equilibrium constant for reaction (1) can be written

$$K = \frac{N_{AmCl_y} \; N_{Pu}^{y/x}}{N_{Am} \; N_{PuCl_x}^{y/x}} \quad \frac{\gamma_{AmCl_y} \; \gamma_{Pu}^{y/x}}{\gamma_{Am} \; \gamma_{PuCl_x}^{y/x}} \quad , \tag{2}$$

where N is the mole fraction and γ is the activity coefficient. The metal phase is essentially pure Pu, so that $N_{Pu} = \gamma_{Pu} = 1$.

The range of Am and $AmCl_y$ concentrations studied varied

from $\sim 2 \times 10^{-4}$ to $\sim 3 \times 10^{-4}$ for N_{AmCl_y} and

from $\sim 5 \times 10^{-5}$ to $\sim 7 \times 10^{-5}$ for N_{Am} .

Therefore, the activity coefficients of Am and $AmCl_y$ should be essentially constant. Further, to a first approximation the activity coefficient of $PuCl_x$ can be assumed to be nearly constant over the mole fraction range studied, 6×10^{-3} to 2×10^{-2}. This is a reasonable assumption since the activity coefficient of $PuCl_3$ has been shown to be constant in the LiCl-KCl system over the $PuCl_3$ mole fraction range 6×10^{-4} to 2×10^{-2}.[5] Equation (2) can therefore be written

$$K' = \frac{N_{AmCl_y}}{N_{Am} \; N_{PuCl_x}^{y/x}} \quad . \tag{3}$$

With the aid of the IBM 7094 computer, values of K' were calculated for each value of x and y from 1 through 6. Typical results are shown in Table 4. In order to observe which values of x and y gave the most constant

Table 4

Equilibrium Constants at 730°C. for

$$Am + \frac{y}{x} PuCl_x = AmCl_y + \frac{y}{x} Pu$$

$N \times 10^2$ $PuCl_3$	$K' \times 10^2$ for $x = 3,\ y = 3$	$x = 3,\ y = 2$
0.658	4.03	0.755
0.688	3.83	0.727
0.764	3.82	0.751
0.767	3.74	0.737
0.836	3.67	0.744
1.02	3.36	0.729
1.03	3.29	0.716
1.08	3.50	0.774
1.41	2.99	0.721
1.64	3.10	0.788
1.69	2.77	0.711
1.76	2.82	0.733
1.82	2.73	0.718
2.13	2.60	0.720
2.39	2.49	0.719
2.50	2.35	0.689
2.53	2.29	0.674

value of K′, the values of K′ for any particular x, y set were normalized by dividing each value of K′ by the maximum value of K′ for that set. The normalized values were then plotted as a function of the weight percent Pu in the salt. A constant value of K′ would therefore result in a straight line plot parallel to the y axis and would intersect the x axis at x = 1.0. The slope of the curve is sensitive to the ratio of y and x. For example almost identical plots can be expected for $PuCl_1$-$AmCl_1$, $PuCl_2$-$AmCl_2$, $PuCl_3$-$AmCl_3$, $PuCl_4$-$AmCl_4$, $PuCl_5$-$AmCl_5$, and $PuCl_6$-$AmCl_6$.

The 36 plots for the experiments at 730°C. are given in the appendix. The same procedure was used for the 698 and 775°C. data. In all cases the most constant value of K′ was obtained for the values (x = 3, y = 2), (x = 6, y = 4), and (x = 5, y = 3).

All previous studies on this type of metal-salt system have shown that trivalent Pu is the only stable Pu ion in equilibrium with Pu metal. Potentiometric measurement in LiCl-KCl have shown that $PuCl_3$ is the only species stable in the presence of Pu metal.[5] Anodic and cathodic efficiency studies in the electrorefining process[1] have indicated that the electrode reactions are

$$Pu^{0} \rightarrow Pu^{+3} \text{ at the anode} \qquad (4)$$

and

$$Pu^{+3} \rightarrow Pu^{0} \text{ at the cathode} \; . \qquad (5)$$

In addition the phase diagram for Pu-$PuCl_3$[6] gives no evidence of a Pu oxidation state other than +3.

The only x, y set consistent with this information is the set x = 3, y = 2. Equation (1) can therefore be written as follows for divalent Am:*

$$Am\ (\ell) + \frac{2}{3} PuCl_3\ (\ell) = AmCl_2\ (\ell) + \frac{2}{3} Pu\ (\ell) \; . \qquad (6)$$

*The conclusion that Am is present in the salt as divalent Am was first reported by Leary and Mullins at the Symposium on Thermodynamics, International Atomic Energy Agency, Vienna, July 22-27, 1965.[7]

Values of K' for reaction (6) for the experiments at 698, 730, and 775°C. are given in Table 5. The average deviations of K' were ±4.5% at 698°C., ±2.0% at 730°C., and ±4.1% at 775°C. These values approximate the expected experimental deviation of 4%. A plot of log K' vs. 1/T gives a ΔH^{o} for reaction (6) of -3.5 kcal.

Since Am is the homolog of Eu and Eu is known to form divalent salts, the presence of divalent Am in the NaCl-KCl salt is reasonable. Although all attempts to prepare pure Am^{+2} compounds have been unsuccessful,[8] the stabilization of divalent Am in a CaF_2 lattice has been postulated recently by workers at the Lawrence Radiation Laboratory.[9] Single crystals of CaF_2 containing 0.1 - 0.2 wt. % AmF_3 were reduced electrolytically at 600°C. Optical absorption spectra of the crystals at room temperature showed the disappearance of the Am^{+3} lines around 5000 Å and the appearance of broad adsorption peaks which were attributed to Am^{+2}.

Table 5

Equilibrium Constants for the Reaction

$$Am + \frac{2}{3} PuCl_3 = AmCl_2 + \frac{2}{3} Pu$$

Temp., °C.	K′ (Avg. Dev.)
698	77.2 (± 3.5)
730	73.0 (± 1.5)
775	67.6 (± 2.8)

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APPENDIX

Plots of $K'/K'_{max.}$ as a function of wt. % Pu in the salt phase for the 730°C. distribution experiments are given in Figs. 2 through 7. $K'/K'_{max.}$ is plotted on the x axis and wt. % Pu in the salt is plotted on the y axis.

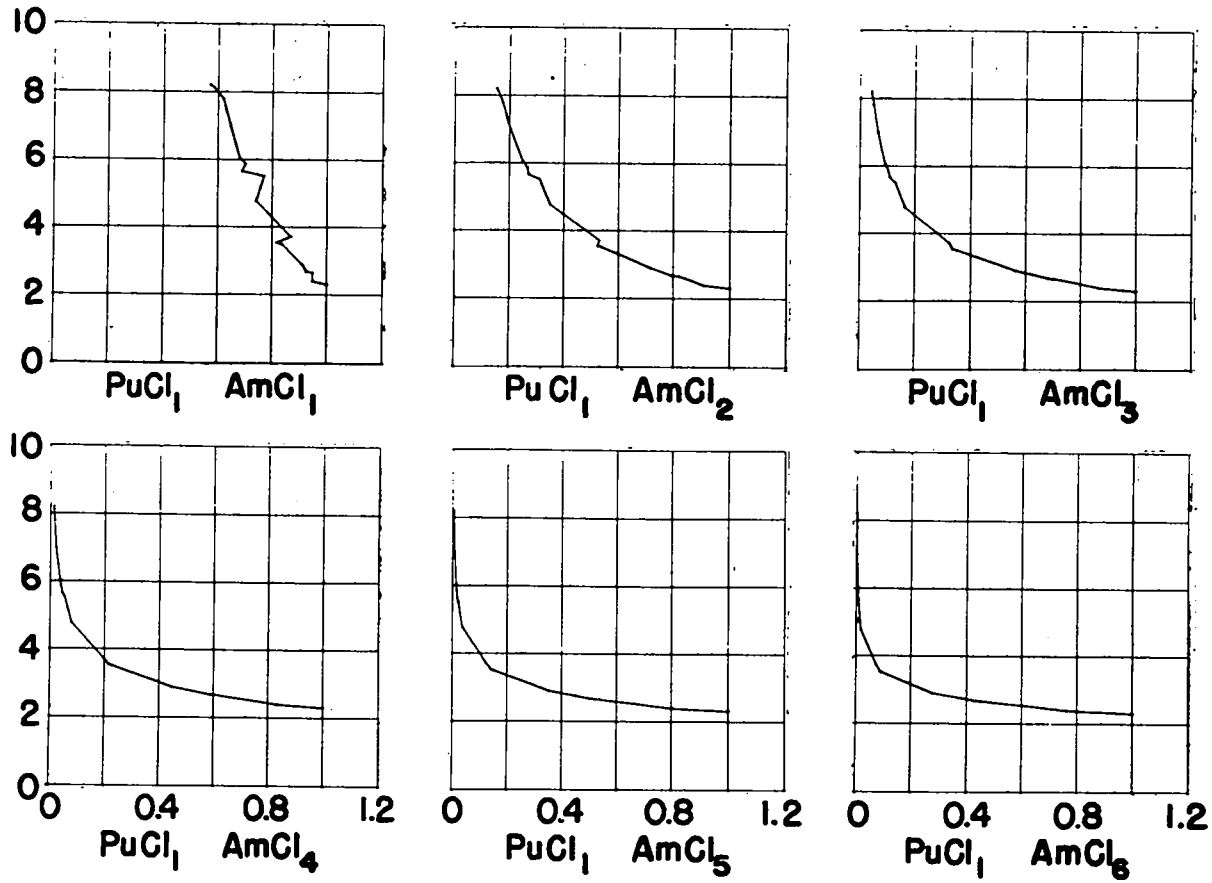

Fig. 2. $K'/K'_{max.}$ (x axis) vs. wt. % Pu in Salt (y axis), 730°C., for the Stoichiometry $PuCl_1$ and $AmCl_1$ through $AmCl_6$

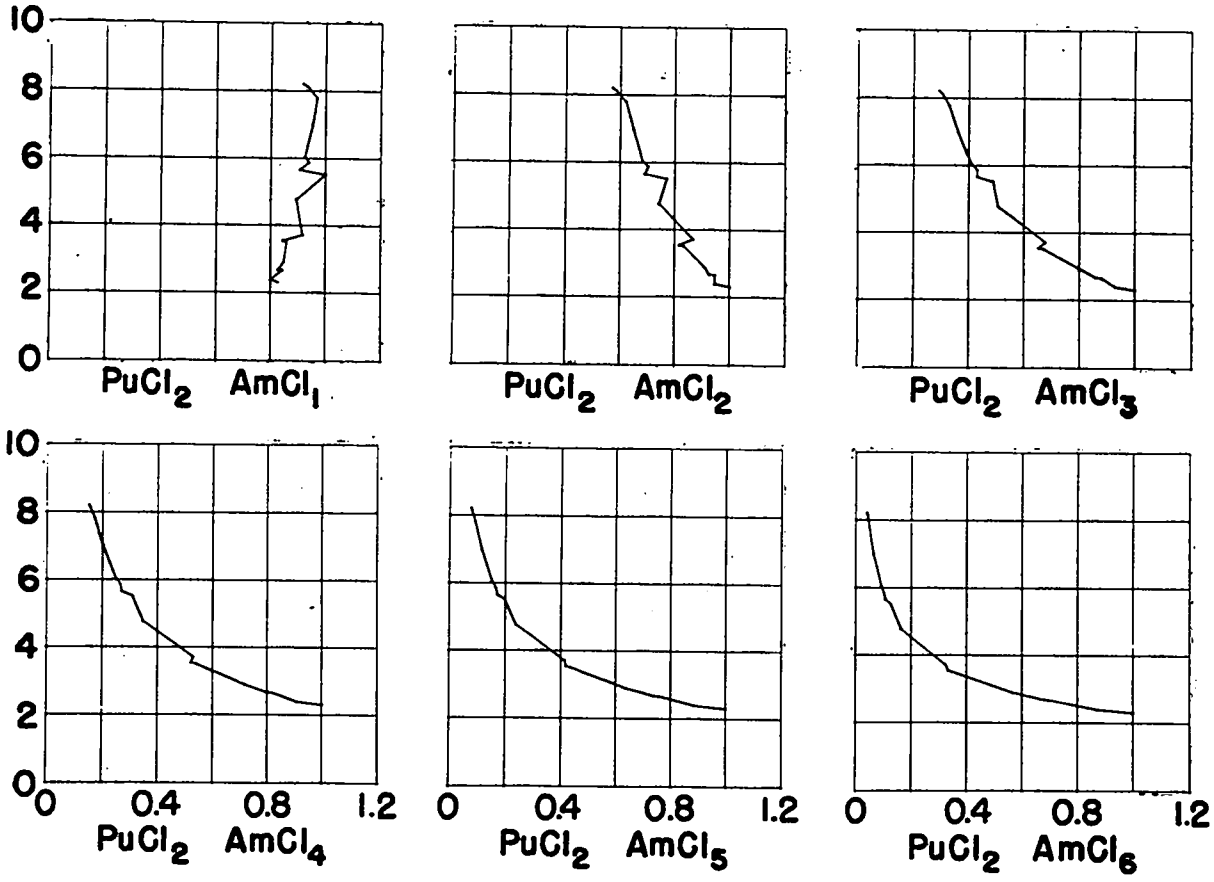

Fig. 3. $K'/K'_{max.}$ (x axis) vs. wt. % Pu in Salt (y axis), 730°C., for the Stoichiometry $PuCl_2$ and $AmCl_1$ through $AmCl_6$

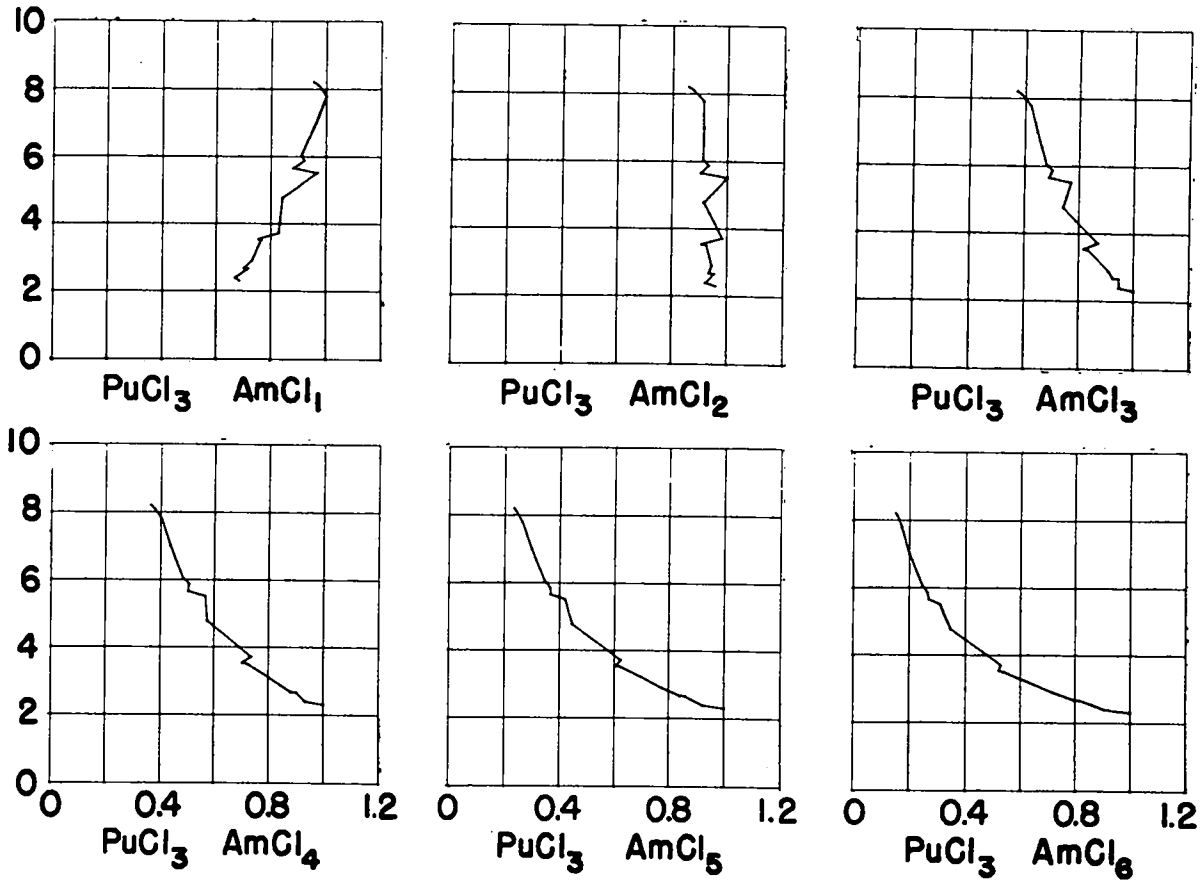

Fig. 4. $K'/K'_{max.}$ (x axis) vs. wt. % Pu in Salt (y axis), 730°C., for the Stoichiometry $PuCl_3$ and $AmCl_1$ through $AmCl_6$

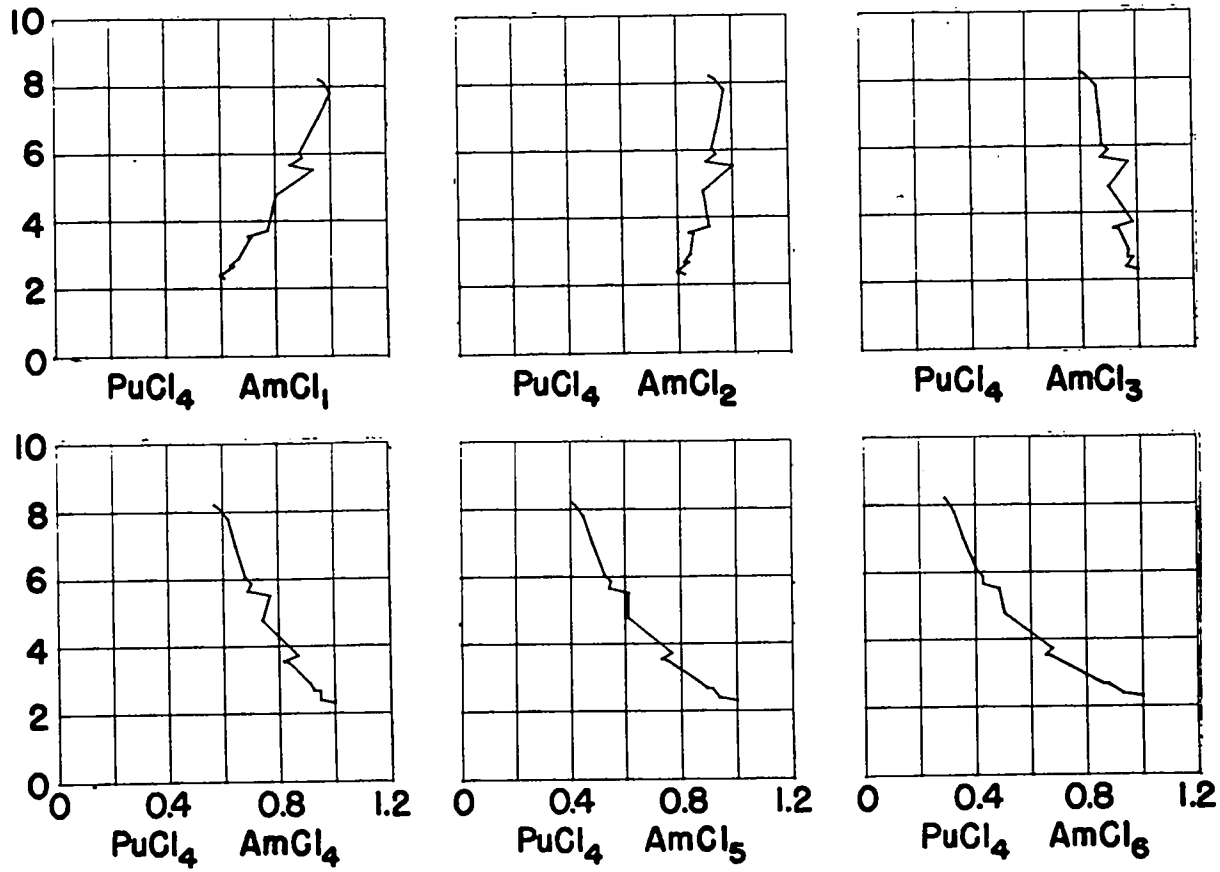

Fig. 5. $K'/K'_{max.}$ (x axis) vs. wt. % Pu in Salt (y axis), 730°C., for the Stoichiometry $PuCl_4$ and $AmCl_1$ through $AmCl_6$

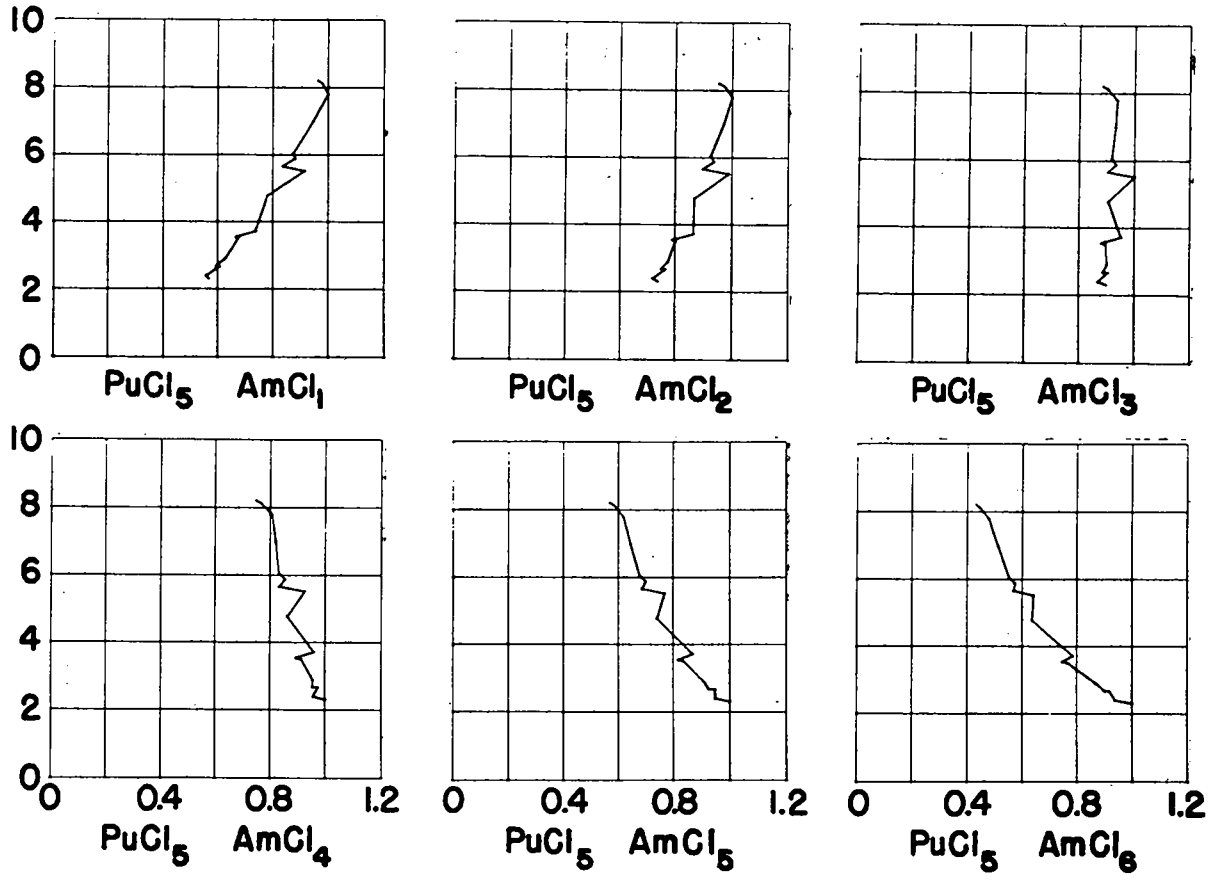

Fig. 6. $K'/K'_{max.}$ (x axis) vs. wt. % Pu in Salt (y axis), 730°C., for the Stoichiometry $PuCl_5$ and $AmCl_1$ through $AmCl_6$

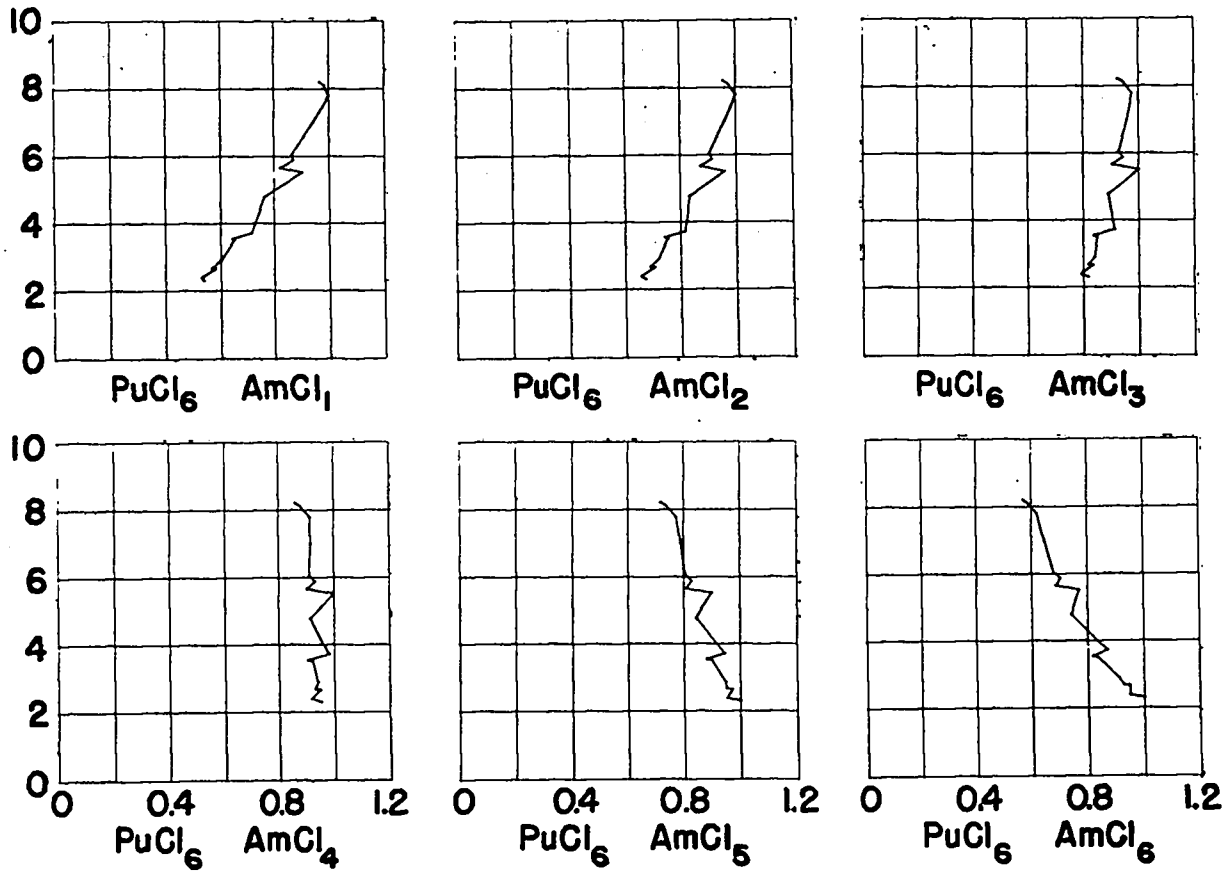

Fig. 7. $K'/K'_{max.}$ (x axis) vs. wt. % Pu in Salt (y axis), 730°C., for the Stoichiometry $PuCl_6$ and $AmCl_1$ through $AmCl_6$