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The Reduction of Uranium Bromide by Molten Aluminum from Fused Potassium Bromide-Aluminum Bromide Mixtures¹

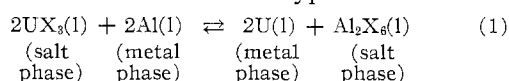
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The reduction of UBr_3 from its solutions in molten $KBr-AlBr_3$ by molten aluminum yields dilute uranium-aluminum alloys by an equilibrium-controlled reaction. The position of the equilibrium is much less favorable for reduction of uranium than the analogous chloride system. In the transition from a pure chloride system to a pure bromide system the position of the equilibrium does not change uniformly but exhibits a marked shift favoring reduction to uranium at low bromide ion concentrations. These phenomena are interpreted in terms of complex ion formation.

Introduction

The molten ternary system $2KX-Al_2X_6-Al$ (where $X = Cl$ or Br) provides a useful two-phase medium in which to conduct reactions of the type



with $X = Cl$, $\Delta F(1000^\circ) = +41.2 \pm 3.1$ kcal. Constituents from both phases play an active role in the reaction.

Where $X = Cl$, it has been shown that eq. 1 does not adequately represent the true reaction conditions since no account is taken of the presence of KCl .^{2,3} When the mole ratio $AlCl_3/KCl = R < 1$, the uranium species in the salt phase has been identified spectrophotometrically as the complex ion, UCl_6^{-3} .⁴ When $R > 1$, the uranium species has not been completely identified, though its spectrum differs from that of UCl_3 or UCl_6^{-3} . Only when $R = 1.0$ is the uranium species UCl_3 , and in this case it is extremely insoluble in the melt and precipitates.

With $X = Cl$, it was shown that reduction of uranium reached a maximum at $R = 1.0$ and decreased at R greater than or less than unity. This behavior is due to the fact that the activity coefficient for the uranium species is unity at $R = 1.0$ (where pure UCl_3 is taken as the standard state) and less than unity as a result of complex formation at R greater than or less than unity. However, the equilibrium of eq. 1 lies markedly to the left (assuming unit activity for all species) and it is impossible to account for nearly complete reduction of UCl_3 by Al at $R = 1.0$, *e.g.*, unless the activity coefficients of U (metal phase) and Al_2Cl_6 (salt phase) are much less than unity.

The activity coefficient of uranium in molten aluminum is about 1.4×10^{-3} at 725° and is reasonably constant over the concentrations applicable here.⁵ The activity coefficient for uranium is not small enough to shift the equilibrium (reaction 1) appreciably to the right.

The vapor pressure of Al_2Cl_6 at 725° is of the order of 10^5 atm. In the range $R = 1.0-1.90$, it was possible to perform experiments in sealed ampoules which would withstand no more than a few atmospheres pressure.² It therefore seemed necessary to attribute the reduction of uranium to the unusual stability of the aluminum chloride complexes with KCl . The species $Al_2Cl_7^-$ and $AlCl_4^-$ were postulated. The species $Al_2Cl_7^-$ is reasonable since 1 mole of KCl effectively stabilizes Al_2Cl_6 . The species $AlCl_4^-$ is supported by X-ray studies of Baenziger.⁶

It was the purpose of work reported here to determine whether the behavior of the bromide system parallels the behavior of the chloride system. The solvent in this case was molten $KBr-AlBr_3$. The behavior of the system in transition from pure chloride to pure bromide was also investigated.

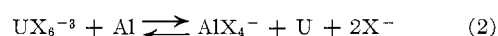
Experimental

The procedure employed in this work differed from that described earlier in that the salt-metal equilibrations were performed in open Vycor tubes instead of in sealed ampoules. This had the disadvantage that slight hydrolysis of the salt phase occurred with production of Al_2O_3 , evident as a slight turbidity. Al_2O_3 does not participate in the equilibrium under study, but its formation alters the $AlCl_3/KCl$ mole ratio, necessitating direct assay for Al and K . The analytical error introduced is of the order of 1-2%.

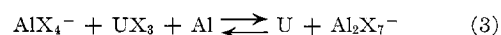
Aluminum is completely immiscible with the salt phase and does not trap the salt phase on cooling, permitting sharp phase separation. Corrosion of the Vycor tube by molten aluminum was not sufficient to affect the results.

Results and Discussion

With the evidence for complex ion formation at hand, eq. 1 is no longer applicable. In a region where $R < 1.0$, eq. 1 becomes



and when $R > 1.0$, eq. 1 becomes



The results of measurements of the distribution of uranium between salt and metal phases at 725° at values of R ranging from 0.20 to 1.07 are shown in Table I. The distribution coefficient, D , is defined

(1) Work performed under Contract No. AT(45-1)-1350 for the U. S. Atomic Energy Commission.

(2) R. H. Moore, J. R. Morrey, and E. E. Voiland, *J. Phys. Chem.*, **67**, 744 (1963).

(3) J. R. Morrey and R. H. Moore, *ibid.*, **67**, 748 (1963).

(4) J. R. Morrey and J. B. Gruber, to be published.

(5) F. Cafasso, private communication.

(6) N. C. Baenziger, *Acta Cryst.*, **4**, 216 (1951).

simply as

$$D = \frac{(X_U)_m}{(X_U)_s} \quad (4)$$

where $(X_U)_m$ and $(X_U)_s$ are the concentrations of uranium in the metal and salt phases, respectively, in mole (ion) fraction units. Though the data in the region where $R > 1.0$ are limited to a single example, it is evident that the distribution coefficient attains a maximum near a mole ratio of unity, as was the case in the chloride system. Further $U\text{Br}_3$ reduction is much less extensive than that of $U\text{Cl}_3$ at comparable values of R .

TABLE I
DISTRIBUTION DATA FOR URANIUM AT 725° IN THE SYSTEM
 $2\text{KBr}-\text{Al}_2\text{Br}_6-\text{Al}^a$

R	D (exptl.)	K_2'
0.20	0.011	8.15×10^{-4}
0.46	0.011	4.74×10^{-4}
0.45	0.014	6.25×10^{-4}
0.63	0.029	5.78×10^{-4}
0.60	0.033	7.73×10^{-4}
0.81	0.078	3.85×10^{-4}
0.76	0.051	4.10×10^{-4}
0.78	0.067	4.48×10^{-4}
0.88	0.25	4.77×10^{-4}
0.95	0.36	1.15×10^{-4}
		Av. 5.1×10^{-4}
1.07	0.21	0.016 ^b

^a From the Cl^- system,² $K_2' = 4.7 \times 10^{-3}$ and $K_3' = 0.35$.

^b K_3' , calcd., from eq. 13.

With the assumption of complex ion formation, eq. 1 no longer applies. It is instructive, however, to explore the relationship between D and the equilibrium constant for reaction 1, K , where

$$K = \frac{A_U^2 A_{\text{Al}_2\text{X}_6}}{A_{\text{UX}_3}^2 A_{\text{Al}}^2} = \frac{X_U^2 X_{\text{Al}_2\text{X}_6} f_U^2 f_{\text{Al}_2\text{X}_6}}{X_{\text{UX}_3}^2 X_{\text{Al}}^2 f_{\text{UX}_3}^2 f_{\text{Al}}^2} \quad (5)$$

In eq. 5, the A 's are activities, the X 's indicate mole fractions, and the f 's are activity coefficients. In this work, X_U was always low. The activity of aluminum may therefore be approximated as unity if pure aluminum is chosen as the standard state. The activity coefficient of uranium is nearly constant. Taking account of eq. 4, eq. 5 reduces to

$$K' = D X_{\text{Al}_2\text{X}_6} \frac{f_{\text{Al}_2\text{X}_6}}{f_{\text{UX}_3}^2} \quad (6)$$

Equation 6 reveals that deviations from ideal behavior are primarily the result of the concentration dependence of the activity coefficients of Al_2X_6 and UX_3 .

Comparing the chloride and bromide systems with reference to eq. 6, it seems unlikely in such dilute salt solutions that differences in the activity coefficients of $U\text{Cl}_3$ and $U\text{Br}_3$ can be sufficient to account for the observed differences in D . Little is known, however, about the nature of $U\text{Br}_3$ solutions of this kind and it is necessary to explore, in more detail, a comparison with the chloride system.

In ref. 2 it was shown that the equilibrium constant

for reaction 2 can be written

$$K_2' = \frac{X_{\text{AlX}_4^-} X_U X_{\text{X}^-}^2}{X_{\text{UX}_3} X_{\text{Al}}} \quad (7)$$

where the X 's are mole (ion) fractions and activity coefficients are assumed to be unity or constant. The mole fraction of aluminum was greater than 0.99 in all experiments and may be considered unity, and with the assumption that all of the uranium in the salt phase was present as UX_3 , eq. 7 becomes

$$K_2' = D X_{\text{AlX}_4^-} X_{\text{Cl}^-}^2 \quad (8)$$

where D is defined by eq. 4.

The values of $X_{\text{AlX}_4^-}$ and X_{Cl^-} can be determined from R , the mole ratio Al/K , *i.e.*

$$X_{\text{AlX}_4^-} = R/2 \quad (9)$$

$$X_{\text{X}^-} = (1 - R)/2 \quad (10)$$

Substituting in eq. 6

$$K_2' = (D/8) [R(1 - R)^2] \quad (11)$$

and

$$D_2 = \frac{8K_2'}{R(1 - R)^2} \quad (12)$$

where D_2 is the calculated distribution coefficient.

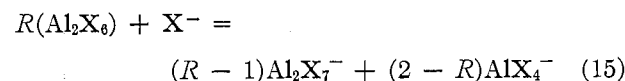
With Al_2X_6 in excess, eq. 3 applies. With the same assumptions as above, here

$$K_3' = \frac{X_U X_{\text{Al}_2\text{X}_7^-}}{X_{\text{AlX}_4^-} X_{\text{UX}_3} X_{\text{Al}}} \quad (13)$$

and

$$K_3' = \frac{X_{\text{Al}_2\text{X}_7^-}}{X_{\text{AlCl}_4^-}} D \quad (14)$$

In a system prepared from R moles of Al_2X_6 and 1 g.-ion of halide, X^- , AlX_4^- , and Al_2X_7^- will form according to the equation



hence

$$\frac{X_{\text{Al}_2\text{X}_7^-}}{X_{\text{AlX}_4^-}} = \frac{(R - 1)}{(2 - R)} \quad (16)$$

Substituting into eq. 14 results in

$$K_3' = \frac{D(R - 1)}{(2 - R)} \quad (17)$$

and

$$D_3 = \frac{K_3'(2 - R)}{(R - 1)} \quad (18)$$

For these equilibrium constants the prime emphasizes that these are not the thermodynamic equilibrium constants but are related to it by a constant factor.

The equilibrium constants calculated from eq. 11 and 17 are shown in Table I. Reasonably constant values

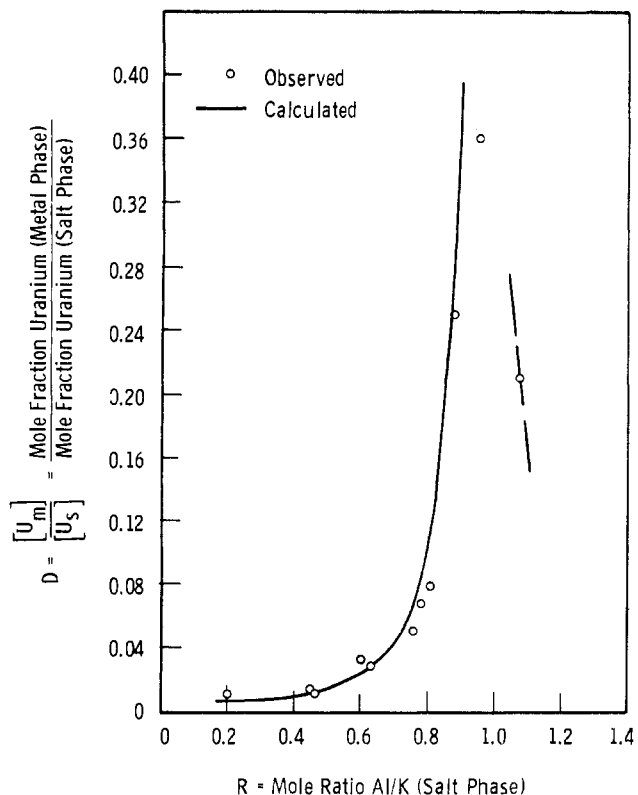


Fig. 1.—Distribution of uranium in the system KBr-AlBr₃-Al at 725°.

are obtained. The average values are compared with the average K values obtained for the chloride system.² The distribution coefficients calculated from eq. 12 and 18, using the average K values, were used to establish the solid and dashed curves of Fig. 1. The circles are experimental distribution data. The agreement is taken as evidence that the bromide system fits the proposed model just as was the case for the chloride system, at least in the region where excess bromide ion is present. The data are not sufficient to establish this where Al₂Br₆ is present in excess.

The uranium species undergoes less reduction in the bromide system than in the chloride system at all values of R . When $R = 1.0$, UCl₆⁻³ converts to UCl₃, indicating that the chloride complexes of aluminum are more stable than those of uranium. Uncomplexed UCl₃ is insoluble and forms a precipitate in the absence of aluminum. With aluminum present, reduction to uranium is nearly complete. This reaction is driven by formation of the AlCl₄⁻ ion. Since the behavior of UBr₃ seems to parallel that of UCl₃ in all other respects, it seems probable that uncomplexed UBr₃ is also formed at $R = 1.0$. Its failure to be reduced as completely as UCl₃ indicates that formation of AlBr₄⁻ does not provide as much driving force as does formation of AlCl₄⁻, *i.e.*, AlCl₄⁻ is more stable than AlBr₄⁻, in agreement with ion size and electronegativity considerations.

When small amounts of bromide ion are substituted for a portion of the chloride ion at values of R slightly greater than 1.0, a marked increase in uranium reduc-

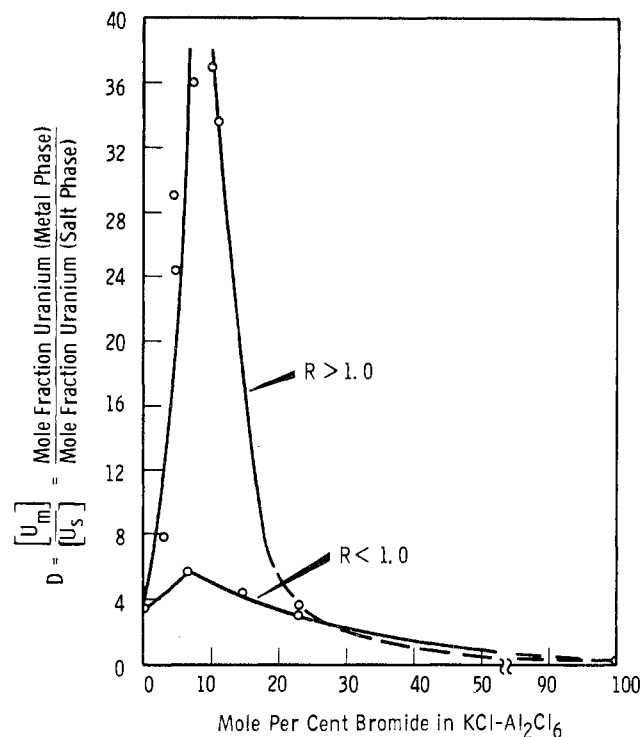
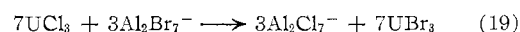


Fig. 2.—Effect of bromide ion on the distribution of uranium in KCl-Al₂Cl₆-Al at 725°.

tion occurs, as shown in Fig. 2. These additions of bromide ion (added as KBr-AlBr₃ with R slightly greater than 1.0) produce a competition between UCl₃ and Al₂Cl₇⁻ for the added halide. If, as suggested above, the complex chloride ions are more stable than the analogous bromide ions, the following metathesis reaction should result.



In this situation the driving force for reduction is the same as in a pure chloride system, *i.e.*, Al₂Cl₇⁻ formation. The enhanced reduction observed must be attributed to the lesser stability of UBr₃ as compared with UCl₃, as is indicated by their free energies of formation. This effect cannot be due to differences in activity coefficients of UBr₃ and UCl₃ because $f_{\text{UX}_3} \approx 1.0$ in this case.

When $R < 1.0$, this effect virtually disappears (Fig. 2). That it was observed at all was unexpected, because UCl₆⁻³ should be more stable than UBr₆⁻³ which should, therefore, have little tendency to form in systems containing excess Cl⁻.

Conclusions

These distribution data constitute an extension of earlier studies^{2,3} and, together with references cited, show that the complex bromo anions of aluminum are less stable than the analogous chloro anions. This accounts for the less efficient reduction of UBr₃ and its complex ions from the pure bromide system. Measurements in mixed chloride-bromide systems have been interpreted to show that UBr₃ is more readily reduced than UCl₃, as predicted from free energy considerations.