

THE ELECTROCHEMISTRY OF BATHS OF FUSED
ALUMINUM HALIDES. IIIBROMIDE BATHS^{1, 2}RALPH WEHRMANN AND J. F. YNTEMA³*Department of Chemistry, St. Louis University, St. Louis, Missouri**Received May 23, 1944*

The solubilities of metal bromides in anhydrous aluminum bromide and the high conductivities of the resulting mixtures in the fused state have been reported by a number of investigators (2, 4, 6, 8). These mixtures are characterized by low melting points. Izbekov (5) and others (1, 3, 10) have determined the decomposition potentials of various metal bromides dissolved in aluminum bromide alone or admixed with alkali bromides. Deposition potentials have also been measured.

Various reference electrodes have been used in the measurement of deposition potentials in fused halide melts, among which are the following: a mercurous chloride electrode (1) in an aluminum bromide-potassium bromide bath; a sodium electrode (10) in an aluminum bromide-sodium bromide bath; and a platinum electrode (13) and an aluminum electrode (12) in an aluminum chloride-sodium chloride-potassium chloride bath. The aluminum reference electrode, consisting of a rod of pure aluminum, has been shown to be reversible and reproducible. It cannot be used, of course, to determine the potentials of metals more active than aluminum. Because the absolute value of the potential of this electrode is not known, the potentials obtained by its use are only comparative.

Yntema and coworkers (9, 11, 12, 13) have determined the deposition potentials of most of the heavy metals from solutions of their chlorides in an aluminum chloride-sodium chloride-potassium chloride bath and also the decomposition potentials of such solutions. The present work, also using the aluminum reference electrode, extends the study to analogous bromide baths and to mixed chloride-bromide baths.

APPARATUS AND PROCEDURE

The apparatus and experimental techniques have been described previously (12). The bath used as the solvent for the metal bromides consisted of 58.68 g. of aluminum bromide (66 mole per cent), 6.86 g. of sodium bromide (20 mole per cent), and 5.55 g. of potassium bromide (14 mole per cent). These mole percentages are the same as those of the corresponding chlorides in the previous work.

¹ For earlier papers in this series see *J. Phys. Chem.* **46**, 344-58 (1942).

² This paper constitutes a portion of a dissertation submitted by Ralph Wehrmann to the Faculty of the Graduate School of St. Louis University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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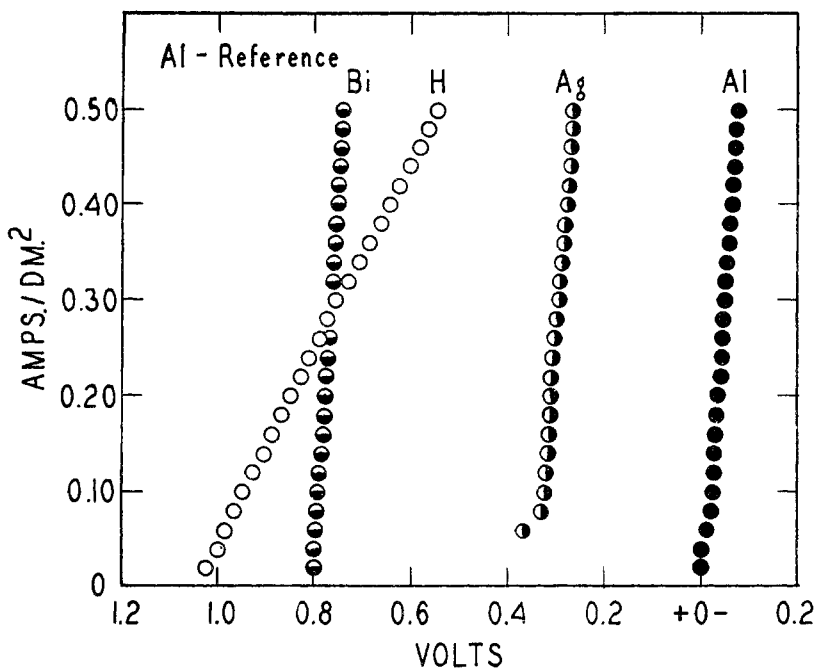


FIG. 1. Deposition potentials. *I* versus *E* (measured from aluminum reference electrode to cathode). Aluminum bromide-potassium bromide-sodium bromide bath. Concentration of metals, 1 mole per cent; temperature, 218°C.; lower current densities.

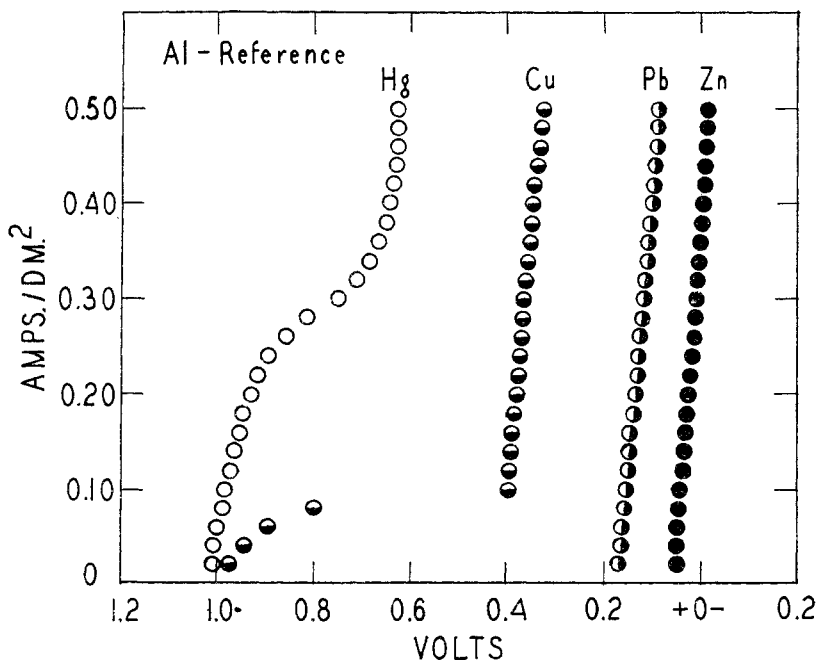


FIG. 2. Deposition potentials. *I* versus *E* (measured from aluminum reference electrode to cathode). Aluminum bromide-potassium bromide-sodium bromide bath. Concentration of metals, 1 mole per cent; temperature, 218°C.; lower current densities.

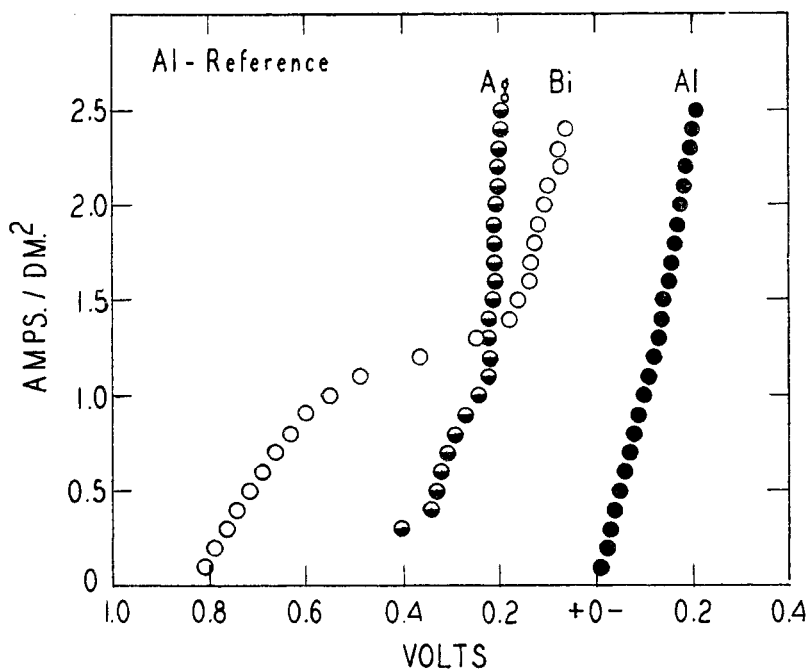


FIG. 3. Deposition potentials. I versus E (measured from aluminum reference electrode to cathode). Aluminum bromide-potassium bromide-sodium bromide bath. Concentration of metals, 1 mole per cent; temperature, 218°C.; higher current densities.

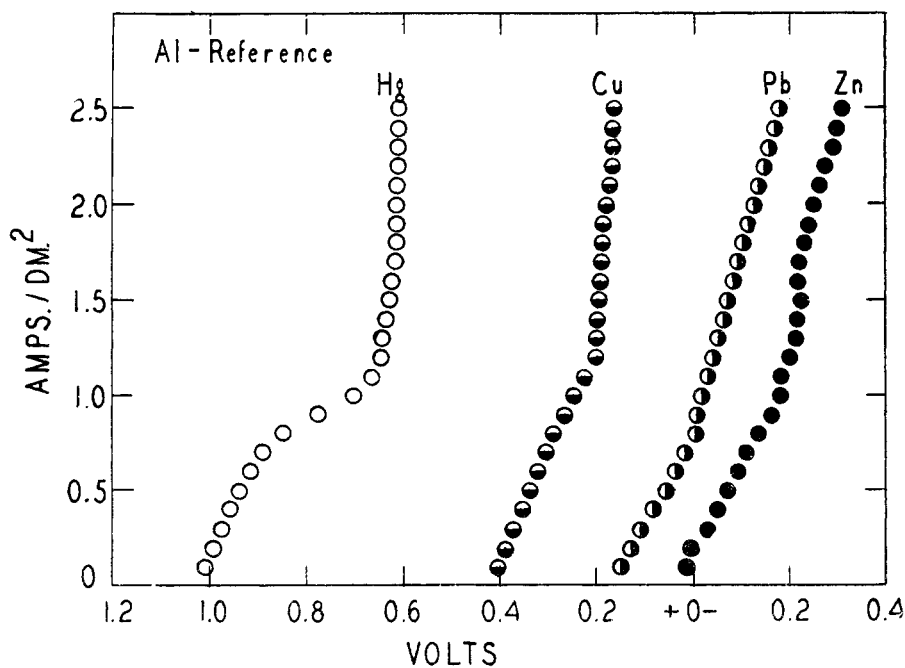


FIG. 4. Deposition potentials. I versus E (measured from aluminum reference electrode to cathode). Aluminum bromide-potassium bromide-sodium bromide bath. Concentration of metals, 1 mole per cent; temperature, 218°C.; higher current densities.

REAGENTS

Anhydrous aluminum bromide was prepared by direct combination of the elements, according to a procedure described by Kaveler and Monroe (7). Bromine, analytical reagent grade diluted with hydrogen or nitrogen, was passed over aluminum at 400°C. The use of the diluent gas facilitated the removal of the product from the reaction zone. After refluxing in a stream of pure nitrogen, the compound was twice distilled. The final distillation yielded a white, crystalline product.

The metal halides of analytical reagent grade were made anhydrous by heating at 110°C. in stream of dry nitrogen.

EXPERIMENTAL PROCEDURE

All the data reported in this paper were obtained at a bath temperature of 218°C., naphthalene being used in the vapor thermostat. The data for the determination of the decomposition potentials were obtained by measuring the potential drop between cathode and anode at various current densities. The deposition potentials were obtained by measuring the potential drop between the cathode and the aluminum reference electrode. The reference electrode is negative with respect to the more noble metal being deposited.

Potentials were obtained by the direct method; the values were taken from I versus E plots by extrapolation to zero current. Measurements were made through two current density ranges. At lower current densities the current was increased by 0.02 ampere per dm.² increments up to 0.5 ampere per dm.² At the higher current densities the increments were 0.1 ampere per dm.² up to 2.5 amperes per dm.²

ALUMINUM BROMIDE-ALKALI BROMIDE BATHS (SEE TABLE 1)

Aluminum. The series of determinations which were made on the bath without the addition of a "foreign" bromide show the reproducibility of the measurements and the reversibility of the aluminum reference electrode. A value of 1.61 volts was found for the decomposition potential. The value of -0.015 volt for the deposition potential is in good agreement with the value of -0.02 volt reported for the corresponding chloride bath. The deviation from zero may be expected as due to polarization effects.

At low current densities smooth adherent deposits were obtained and at higher current densities needle-like crystals were formed.

Hydrogen. The preparation and maintenance of a bath containing 1 mole per cent of hydrogen was difficult. Two procedures were attempted: 0.80 g. of aluminum chloride hexahydrate was added to the melt. A rather violent reaction ensued, liberating considerable quantities of the hydrogen halides so that the actual hydrogen concentration of the solution was less than the calculated 1 mole per cent. In a second experiment anhydrous hydrogen chloride was bubbled into the bath for 2 hr. before potential measurements were taken. The potential values obtained by the two methods agreed quite closely. The average value for the deposition of hydrogen is +1.05 volts. The same value is reported for the

TABLE I
Deposition potentials and decomposition potentials

Aluminum bromide-sodium bromide-potassium bromide bath; 1 mole per cent solutions; temperature, 218°C.; a, values from measurements at lower current densities; b, values from measurements at higher current densities

ELEMENT	I DEPOSITION POTENTIAL (CATHODE VS. ALUMINUM)	II DECOMPOSITION POTENTIAL (CATHODE VS. ANODE)	SUM OF I AND II
Aluminum.....	-0.02 a	1.60 a	
	0.01 a	1.59 a	
	0.02 a	1.61 a	
	0.01 a	1.60 a	
	0.02 b	1.60 b	
	0.01 b	1.60 b	
	0.01 b*	1.61 b*	
	0.03 b*	1.65 b*	
Mean.....	-0.02	1.61	1.59
Hydrogen.....	+1.06 a	0.51 a	
	1.04 a	0.54 a	
	1.05 a	0.58 a	
	1.04 a	0.50 a	
	1.03 a	0.53 a	
	1.04 a	0.52 a	
Mean.....	+1.05	0.53	1.58
Copper.....	+0.41 a	1.17 a	
	0.41 a	1.19 a	
	0.41 a	1.17 a	
	0.40 a	1.17 a	
	0.41 b	1.13 b	
	0.42 b	1.15 b	
	0.43 b	1.17 b	
Mean.....	+0.41	1.17	1.58
Silver.....	+0.36 a	1.23 a	
	0.37 a	1.23 a	
	0.35 a	1.21 a	
	0.35 b	1.20 b	
	0.41 b	1.25 b	
	0.35 b	1.19 b	
Mean.....	+0.37	1.22	1.59
Zinc.....	+0.04 a	1.56 a	
	0.06 a	1.54 a	
	0.05 a	1.54 a	
	0.04 b	1.58 b	
Mean.....	+0.05	1.56	1.61

TABLE 1—Continued

ELEMENT	I DEPOSITION POTENTIAL (CATHODE vs. ALUMINUM)	II DECOMPOSITION POTENTIAL (CATHODE vs. ANODE)	SUM OF I AND II
Mercury.....	+0.66 a	0.99 a	
	0.66 a	0.98 a	
	0.65 b	1.00 b	
	0.66 b	0.99 b	
Mean.....	+0.66	0.99	1.65
(Reduction potential).....	+1.02 a	0.58 a	
	0.99 a	0.54 a	
	1.04 b	0.59 b	
	1.02 b	0.57 b	
Mean.....	+1.02	0.57	1.59
Lead.....	+0.17 a	1.45 a	
	0.17 a	1.44 a	
	0.17 b	1.44 b	
	0.17 b	1.46 b	
Mean.....	+0.17	1.45	1.62
Bismuth.....	+0.32 b	1.24 b	
	0.30 b	1.28 b	
	0.32 b	1.30 b	
Mean.....	+0.31	1.27	1.58
(Reduction potential).....	+0.80 a	0.77 a	
	0.82 a	0.73 a	
	0.85 a	0.80 a	
	0.80 b	0.78 b	
	0.82 b	0.73 b	
	0.83 b	0.76 b	
Mean.....	+0.82	0.76	1.58

* Values from measurements at 156°C.

deposition potential of hydrogen from an aluminum chloride-alkali chloride melt (12). In view of the fact that hydrogen would not be expected to form complexes in either solution, this agreement is not surprising.

Copper: 0.48 g. of cuprous bromide was used. Bright crystalline deposits of metallic copper were obtained. The current density-potential curves extrapolated to +0.41 volt for the deposition potential and to 1.17 volts for the decomposition potential. The lower portion of the aluminum reference-cathode curve which extrapolates to +1.01 volts is interpreted to represent the reduction of cupric to cuprous ions.

Silver: 0.63 g. of anhydrous silver bromide was readily soluble in the bath. Electrolysis produced a crystalline deposit of silver possessing a bright metallic luster. Silver deposits from this bath at a potential of +0.37 volt, and silver bromide decomposes at a potential of 1.22 volts.

Zinc: Zinc bromide was the most soluble metal bromide studied. 0.75 g. dissolved very rapidly. The measured deposition potential was +0.05 volt and the decomposition potential was 1.56 volts. Since these baths were rapidly depleted of zinc and especially so at higher current densities, potential measurements also were made with solutions containing 2 mole per cent of zinc bromide. These values, within the limits of experimental error, agreed with the results obtained from the more dilute solutions.

Mercury: 1 mole per cent (0.93 g.) of mercurous bromide was readily soluble in the anhydrous salt melt. Globules of metallic mercury were obtained by electrolyzing in both current density ranges. Mercury shows a reduction potential at +1.02 volts and a deposition potential at +0.66 volt; the decomposition potential of mercurous bromide is 0.99 volt.

Lead: A 1 mole per cent solution was obtained by adding 1.20 g. of lead bromide to the solvent. Solution was rapid and electrolysis liberated dark colored deposits of the metal. The average deposition and decomposition potentials were +0.17 and 1.45 volts, respectively.

Bismuth: Bismuth oxide was found to be insoluble in the bath. Potential measurements were made with baths containing 1 mole per cent (0.87 g.) of bismuth oxychloride or 1 mole per cent (1.02 g.) of bismuth oxybromide. The observed deposition and decomposition potentials were +0.31 and 1.27 volts, respectively. It is believed that the lower portion of the aluminum reference-cathode curve which extrapolates to a value of +0.82 volt represents a reduction potential of bismuth. A loosely adherent powder was obtained at the cathode.

ALUMINUM CHLORIDE-ALKALI BROMIDE BATHS (SEE TABLE 2)

In order to determine the effect of large concentrations of chlorides in the solvent, baths consisting of 58.66 g. of aluminum chloride (66 mole per cent), 13.72 g. of sodium bromide (20 mole per cent), and 11.11 g. of potassium bromide (14 mole per cent) were also investigated.

Aluminum: By electrolyzing the solvent containing no foreign metal, smooth adherent deposits were obtained at low current densities. At higher current densities crystalline deposits were obtained. For both current density ranges the average of the extrapolated values for the deposition potential of aluminum and the decomposition potential of the aluminum halide were -0.02 and 1.71 volts, respectively.

Silver: 0.96 g. of silver chloride or 1.25 g. of silver bromide was added to the bath. These salts dissolved rapidly. Small variations in the chloride-to-bromide ratio in the bath had no measurable effect on either the deposition potential of silver or the decomposition potential of the bath. The values found were +0.58 volt and 1.12 volts. Silver was deposited as crystalline metal.

Mercury: Baths were prepared by adding 1.57 g. of mercurous chloride or 1.87

TABLE 2

Deposition potentials and decomposition potentials

Aluminum chloride-sodium bromide-potassium bromide bath; 1 mole per cent solutions; temperature, 218°C.; a, values from measurements at lower current densities; b, values from measurements at higher current densities

ELEMENT	I DEPOSITION POTENTIAL (CATHODE VS. ALUMINUM)	II DECOMPOSITION POTENTIAL (CATHODE VS. ANODE)	SUM OF I AND II
Aluminum:			
AlCl ₃	-0.01 a	1.68 a	
	0.02 a	1.70 a	
	0.02 a	1.70 a	
	0.01 a	1.71 a	
	0.02 b	1.70 b	
	0.02 b	1.73 b	
	0.02b*	1.72b*	
	0.02b*	1.70b*	
Mean.....	-0.02	1.71	1.69
Silver:			
AgCl.....	+0.58 a	1.10 a	
	0.59 a	1.10 a	
	0.58 a	1.11 a	
	0.58 b	1.15 b	
	0.59 b	1.13 b	
Mean.....	+0.58	1.12	1.70
AgBr.....	+0.58 a	1.09 a	
	0.58 a	1.13 a	
	0.59 a	1.12 a	
	0.57 b	1.17 b	
	0.58 b	1.10 b	
Mean.....	+0.58	1.12	1.70
Mercury:			
HgCl.....	+0.84 a	0.87 a	
	0.86 a	0.87 a	
	0.85 b	0.89 b	
	0.85 b	0.88 b	
Mean.....	+0.85	0.88	1.73
(Reduction potential)	+1.03 a	0.62 a	
	1.05 a	0.65 a	
	1.04 a	0.66 a	
Mean.....	+1.04	0.64	1.68
HgBr.....	+0.84 b	0.92 b	
	0.87 b	0.88 b	
	0.85 b	0.85 b	

TABLE 2—Continued

ELEMENT	I DEPOSITION POTENTIAL (CATHODE VS. ALUMINUM)	II DECOMPOSITION POTENTIAL (CATHODE VS. ANODE)	SUM OF I AND II
	0.85 b	0.84 b	
Mean.....	+0.85	0.87	1.72
(Reduction potential).....	+1.06 a	0.60 a	
	1.07 a	0.61 a	
	1.09 a	0.62 a	
Mean.....	+1.07	0.61	1.68

* Values from measurements at 156°C.

g. of mercurous bromide. The deposition potential was found to be +0.85 volt and the decomposition potential to be 0.88 volt. There is a reduction potential indicated by the graphs at +1.04 volts.

DISCUSSION

In previous work on aluminum chloride-alkali chloride baths, the anode compartment consisted of a glass tube with a constricted lower end packed with glass wool upon which a layer of granulated aluminum was placed to prevent diffusion of free chlorine into the cathode compartment. When this device was used with bromide baths containing copper or bismuth bromides, the aluminum became coated with the foreign metal. It is probable that both copper and bismuth were present in anion complexes which migrated to the anode compartment.

A correlation pointed out in an earlier paper (12) may also be noted in this work. The decomposition potential of the aluminum bromide-alkali bromide bath was found to be 1.61 volts. The sum of the deposition and decomposition potentials for baths containing other metals is 1.61 ± 0.04 volts. The close agreement among the data also indicates to us that the procedure described and the values reported are trustworthy. The correlation between deposition and decomposition potentials also applies to the reduction potentials and to the potentials observed for the mixed aluminum chloride-alkali bromide baths.

When chloride is substituted for part of the bromide in the bath, values for the potentials are obtained which are intermediate between those obtained with a chloride and a bromide bath.

SUMMARY

1. The aluminum reference electrode is shown to be applicable for the determination of deposition potentials of metals from a fused aluminum bromide-alkali bromide bath.

2. Deposition potentials determined from baths in which the aluminum was introduced as the chloride were considerably higher, of the order of 0.2 volt with mercury and silver, than those obtained from the all-bromide baths.

3. The deposition potentials as measured with the aluminum reference electrode of the metals studied are as follows: aluminum, -0.02 ; zinc, $+0.05$; lead, $+0.17$; bismuth, $+0.31$; silver, $+0.37$; copper, $+0.41$; mercury, $+0.66$; and hydrogen, $+1.05$ volts. This order of deposition is the same as the voltaic series for the aqueous sulfate solutions of these metals, except for the interchanged positions of copper and silver and the location of hydrogen at the noble end of the series.

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THE ELECTROCHEMISTRY OF BATHS OF FUSED ALUMINUM HALIDES. IV

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This communication extends previous studies (9, 11) on the deposition potentials of metals from solutions of their chlorides in an aluminum chloride-alkali chloride bath. The data for a number of additional elements are presented to complete the list of those that can be studied by the procedure.

APPARATUS AND PROCEDURE; REAGENTS

The apparatus and experimental procedures used were the same as those previously described. All reagents were of A.R. or C.P. grade. The chlorides were dehydrated, when necessary, by heating in a current of dry hydrogen chloride. Certain compounds were prepared by standard methods, as indicated.

The electrolysis bath consisted of 58.68 g. of anhydrous aluminum chloride (66 mole per cent), 7.78 g. of sodium chloride (20 mole per cent), and 6.96 g. of potassium chloride (14 mole per cent). A bar of pure aluminum served as reference

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