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.

REFERENCES

(1) Delimars'kii and izbekov: Mem. Inst. Chem. Ukrain. Acad. Sci. **3,** 541 (1936).
(2) Izbekov and Plotnikov: Z. anorg. Chem. **71,** 328 (1911).
(3) Izbekov and Ya Zakharchenko: Mem. Inst. Chem. Ukrain. Acad. Sci. **2,** 121 (1935).
(4) Izbekov: Z. anorg. Chem. **143,** 80 (1925).
(5) Izbekov: Z. physik. Chem. **116,** 304 (1925).
(6) Izbekov: J. Russ. Phys. Chem. Soc. **45,** 1792 (1913).
(7) Kaveler and Monroe: J. Am. Chem. Soc. **50,** 2421 (1928).
(8) Kendall, Crittenden, and Miller: J. Am. Chem. Soc. **45,** 963 (1923).
(9) Marshall and Yntema: J. Phys. Chem. **46,** 353 (1942).
(10) Skobets and Kavetskii: J. Gen. Chem. (U. S. S. R.) **10,** 1858 (1940).
(11) Verdieck, Ralph G.: Thesis, St. Louis University, 1943.
(12) Verdieck and Yntema: J. Phys. Chem. **46,** 344 (1942).
(13) Wade, Twellmeyer, and Yntema: Trans. Electrochem. Soc. **78,** 77 (1940).

THE ELECTROCHEMISTRY OF BATHS OF FUSED ALUMINUM HALIDES. IV

RALPH G. VERDIECK AND L. F. YNTEMA[1]

Department of Chemistry, St. Louis University, St. Louis, Missouri

Received May 23, 1944

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

---

[1] Present address: Fansteel Metallurgical Corporation, North Chicago, Illinois.

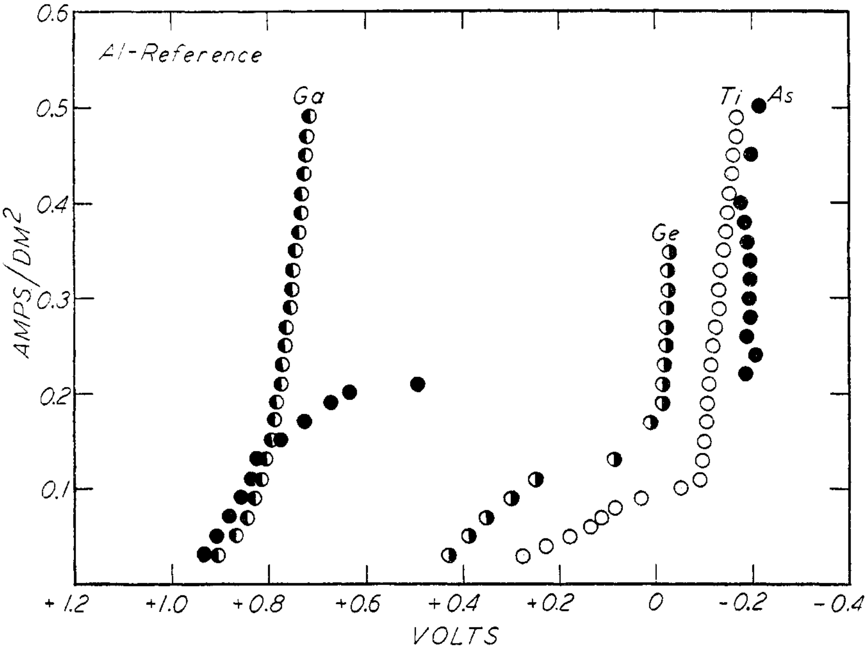

FIG. 1. Deposition potentials. *I versus E* (measured from aluminum reference (electrode to cathode). Concentration of metals, 1 mole per cent; temperature, 156°C.; lower current densities.

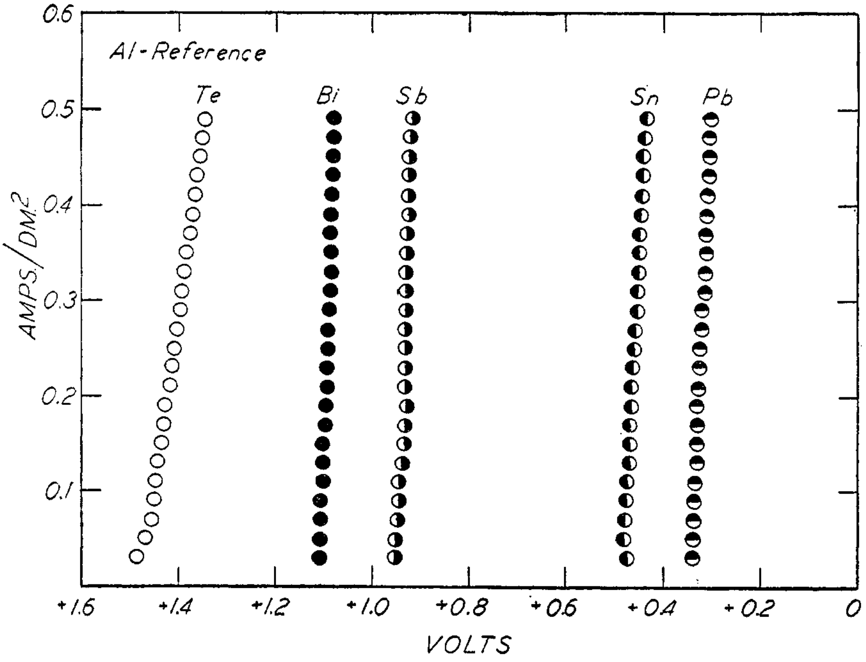

FIG. 2. Deposition potentials. *I versus E* (measured from aluminum reference electrode to cathode). Concentration of metals, 1 mole per cent; temperature, 156°C.; lower current densities.

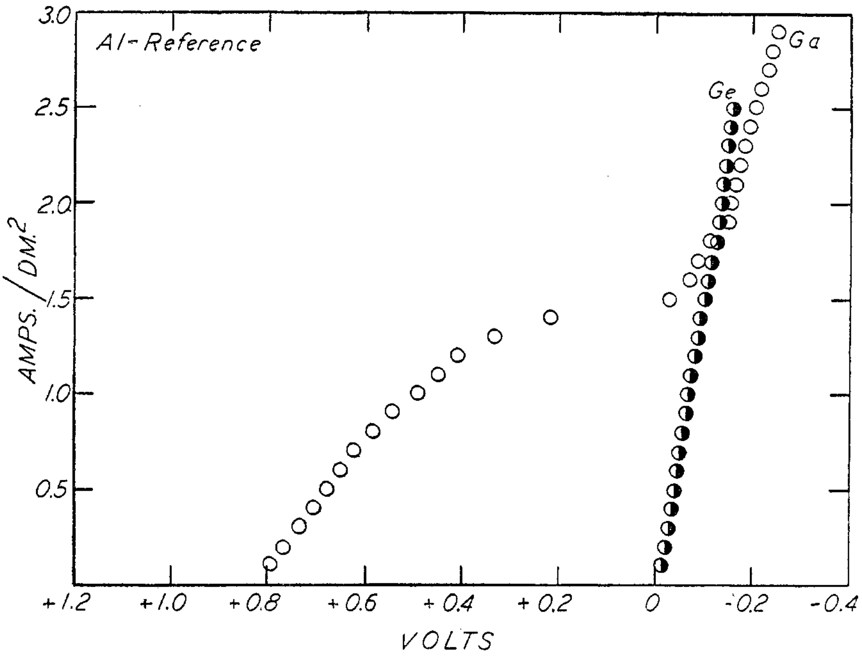

FIG. 3. Deposition potentials. *I versus E* (measured from aluminum reference electrode to cathode). Concentration of metals, 1 mole per cent; temperature, 156°C.; higher current densities.

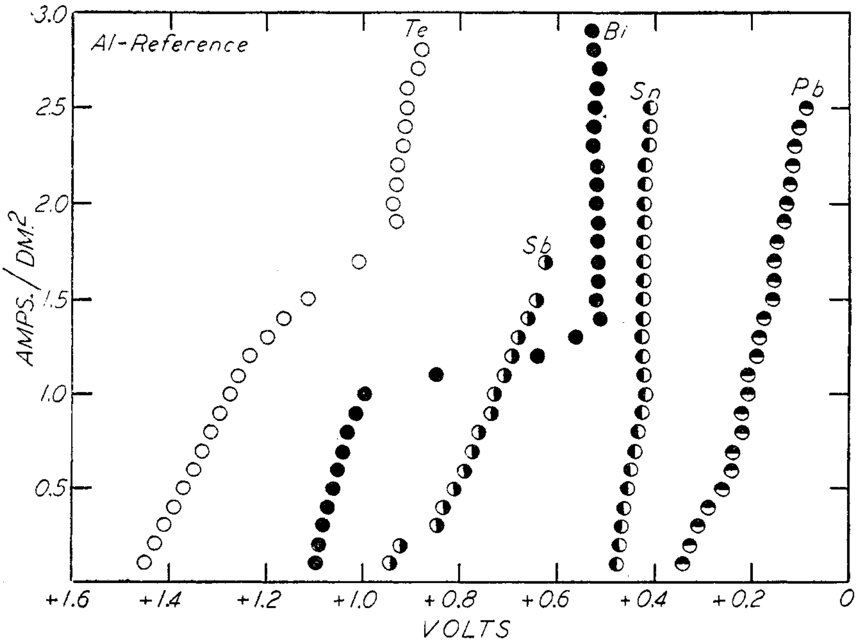

FIG. 4. Deposition potentials. *I versus E* (measured from aluminum reference electrode to cathode). Concentration of metals, 1 mole per cent; temperature, 156°C.; higher current densities.

electrode, and the measured deposition potentials represent the potential difference between the cathode and the aluminum reference electrode. Decomposition potentials were found by measuring the cathode to anode voltage drops.

Typical *I versus E* graphs are given in figures 1, 2, 3, and 4.

RESULTS (SEE TABLE 1)

Gallium: A 1 mole per cent solution of gallium was prepared by adding 1.61 g. of gallic oxide, Ga_2O_3, to the bath. At low current densities a darkening of the cathode occurred, but the deposit contained no gallium. At higher current densities small globules of metallic gallium were deposited.

The extrapolation of the *I versus E* graphs for lower current densities indicates a reduction potential at 0.83 volt. At higher current densities the data do not give regular curves, but a value of approximately 0.2 volt for the deposition potential of the metal is indicated. The decomposition potential appears to be about 2.0 volts.

Thallium: 1.61 g. of thallous chloride was dissolved in the bath. Electrolysis of the solution gave deposits containing aluminum but no thallium. The deposition potential and decomposition potentials were identical with those obtained with a bath without any additions. It is probable that the concentration of free Tl^+ ions in solution is extremely small.

Skobets and Abarbarchuk (10) reported that the deposition potential of thallous chloride in a bath of fused cadmium chloride is the same as that of cadmium chloride, 1.08 volts, indicating that cadmium is deposited at a lower potential than thallium.

Germanium: It was found that germanium dioxide was insoluble in the bath, but that solutions could be prepared by dissolving 1.76 g. of potassium fluogermanate. Electrolysis gave a thin black plate, insoluble in dilute hydrochloric acid. At low current densities there is a reduction potential at 0.50 volt. At higher current densities the deposition potential is -0.01 volt.

The anode to cathode potential is 1.58 volts at low current densities and 2.06 volts at higher current densities.

Tin: Upon electrolysis of a bath containing 1.27 g. of stannous chloride, a bright deposit of metallic tin crystals was obtained. At lower current densities a deposition potential of 0.48 volt was found and at higher current densities a potential of 0.49 volt. At still higher current densities a value of 0.44 volt was found.

The decomposition potential is 1.61 volts at low current densities and 1.62 volts at higher current densities.

Izbekov and Chovnik (4) reported a decomposition potential of 0.74 volt for stannous chloride in a melt of aluminum and potassium chlorides at 250°C. and 0.60 volt at 350°C. Skobets and Abarbarchuk (10) deposited tin from a solution of stannous chloride in molten cadmium chloride and reported the decomposition potential to be 0.56 volt. Drossbach (3) reported the decomposition potential of stannous chloride to be 0.535–0.550 volt at 460°C. Coerver (1), using essentially the same procedure as the authors, found that the deposition potential of tin, referred to metallic aluminum, is 0.47 ± 0.03 volt.

TABLE 1

Deposition potentials and decomposition potentials

1 mole per cent solutions; temperature, 156°C. (except as indicated); a, values from data at lower current densities; b, values from data at higher current densities; potentials marked "R" represent reduction potentials to lower valent forms

ELEMENT	I DEPOSITION POTENTIAL	II DECOMPOSITION POTENTIAL	SUM OF I AND II
Gallium	+0.83 a	1.22 a	
	0.84 a	1.21 a	
	0.80 a		
	0.80 a		
	0.83 a		
	0.84 a		
	0.82 a		
	0.82 a		
	0.86 a		
	0.86 a		
	0.86 a		
	0.86 a		
Mean	0.83 (R)	1.22	2.05
	0.20 b	1.26 b	
	0.20 b	2.0 b	
Mean	0.20	?	
Thallium	−0.01 a	2.06 a	
	0.00 a		
	0.02 b	2.06 b	
	0.02 b		
Mean	0.01	2.06	2.07
Germanium	+0.52	1.58	
	0.50	1.58	
Mean	+0.51 (R)	1.58	2.09
	+0.01 a	2.07 a	
	−0.01 a	2.05 a	
	0.00 b	2.05	
	0.00 b		
Mean	0.00	2.06	2.06
Tin	+0.47 a	1.61 a	
	0.50 a	1.60 a	
	0.48 a	1.60 a	
	0.48 a	1.63 a	
	0.48 a		

TABLE 1—*Continued*

ELEMENT	I DEPOSITION POTENTIALS	II DECOMPOSITION POTENTIALS	SUM OF I AND II
Tin	0.49 a		
	0.49 a		
	0.49 a		
Mean	0.48	1.61	2.09
	0.43 b		
	0.43 b	1.61 b	
	0.44 b	1.62 b	
	0.44 b	1.63 b	
Mean	0.43	1.62	2.05
Lead	+0.37 a	1.76 a	
	0.36 a	1.74 a	
	0.35 a	1.72 a	
	0.37 a	1.74 a	
	0.36 a	1.52 b (?)	
	0.36 a		
	0.36 a		
	0.36 b		
	0.37 b		
	0.36 b		
Mean	0.36	1.74	2.10
Titanium	−0.04 b	2.11 b	
	−0.05 b	2.10 b	
	−0.04 b	2.12 b	
	−0.04 b		
	−0.04 b		
	−0.07 b		
Mean	−0.05	2.11	2.06
Arsenic	+1.01 a	1.10 a	
	0.99 a	1.08 a	
	0.98 a		
	0.96 a		
	0.96 a		
Mean	+0.98	1.09	2.07
Antimony	+0.96 a	1.08 a	
	0.94 a	1.10 a	
	0.95 a		
	0.94 a		
	0.95 a		
	0.94 a		
	0.96 a		
Mean	0.95	1.09	2.04

TABLE 1—*Continued*

ELEMENT	I DEPOSITION POTENTIAL	II DECOMPOSITION POTENTIAL	SUM OF I AND II
Bismuth:			
(Bi_2O_3)	+1.10 a	1.00 a	
	1.11 a	1.00 a	
	1.11 a	1.01 a	
	1.11 a	1.00 a	
	1.11 a	1.01 a	
	1.11 a	1.01 a	
	1.11 a	1.01 a	
Mean	+1.11 (R)	1.01	2.12
	+0.53 b	1.62 b	
	0.50 b	1.62 b	
Mean	0.51	1.62	2.13
$(BiOCl)$	+1.08 a	1.01 b	
	1.08 a		
Mean	+1.08 (R)		
Vanadium:			
$K_2VO_2F_3$	−0.10 a	2.20	
	−0.13 a	2.20	
	−0.12 a		
	−0.10 a		
Mean	−0.11	2.20	2.09
V_2O_5	−0.09 a	2.16 a	
	−0.10 a	2.21 a	
	−0.10 a		
	−0.04 b		
	−0.04 b		
Mean	−0.07	2.19	2.12
Columbium:			
(Cb_2O_5)	+0.03 a	2.08 a	
	0.03 a		
Mean	+0.03		
K_2CbF_7	+0.02 a	2.08 a	
	0.02 a	2.14 a	
	0.02 a	2.08 b	
	0.01 b		
	0.00 b		
	−0.02 b		
Mean	+0.01	2.10	2.11

TABLE 1—*Concluded*

ELEMENT	I DEPOSITION POTENTIAL	II DECOMPOSITION POTENTIAL	SUM OF I AND II
Tantalum	+0.83 a	1.21 a	
	0.84 a		
Mean	+0.84 (R)		
K_2TaF_7	+0.86 a	1.33 a	
	0.85 a	1.30 a	
	0.83 a	1.30 a	
	0.81 a		
	0.85 a		
	0.84 a		
Mean	+0.84 (R)	1.31	2.15
Ta_2O_5	−0.03 b	2.11 b	
	−0.01 b	2.10 b	
	−0.03 b		
	−0.01 b		
Mean	−0.02	2.11	2.09
K_2TaF_7	0.00 b	2.20 b	
	−0.01 b	2.14 b	
	+0.02 b	2.14 b	
	+0.02 b	2.17 b	
	−0.01 b	2.17 b	
	−0.02 b		
	+0.01 b		
	−0.03 b		
	−0.01 b		
	−0.02 b		
Mean	0.00	2.16	2.16
Tellurium	+1.46 a	0.60	
	1.48 a	0.60	
	1.47 a	0.60	
	1.47 a	0.59	
	1.47 a	0.60	
	1.46 a	0.60	
	1.48 a	0.57	
	1.48 a		
Mean	+1.47 (R)	0.60	2.07
	+1.15 b		
	1.02 b		
	1.08 b		
	1.04 b		
Mean	+1.07		

Lead: 1.86 g. of lead chloride was dissolved, and electrolysis at low current densities produced small bright crystals of metal. The deposition potential is 0.36 volt; above 1 ampere cm.^{2} the deposition potential is 0.28 volt. The decomposition potential is 1.74 volts.

Lorenz and Velde (7) measured the E.M.F. in carbon anode–carbon cathode systems at different temperatures and reported a value of $1.2467 - 6.5 \times 10^{-4} (t - 550°)$. Skobets and Abarbarchuk (10) found that the decomposition potential of lead chloride in a melt of cadmium is greater than that of the solvent. Coerver (1), using essentially the same procedure as the authors, found the deposition potential of lead, referred to an aluminum reference electrode, to be 0.34 ± 0.03 volt.

Titanium: The dioxide of titanium is insoluble in the bath. A 1 mole per cent solution was prepared by dissolving 1.59 g. of potassium fluotitanate. No deposits were formed on the cathode at potentials lower than those required for the deposition of aluminum. At higher potentials a black deposit, interspersed with a white non-adherent material, was formed. The black deposit was soluble in hot concentrated sulfuric acid, forming a solution containing titanium ions.

The deposition potential of titanium from the solution is higher than that of aluminum, −0.05 volt, and the decomposition potential of the solution is 2.11 volts.

Arsenic: 0.66 g. of arsenious oxide was used. Metallic arsenic plated out as a jet-black, bright deposit at 0.98 volt at low current densities. At higher current densities, arsenic and aluminum were deposited together. The decomposition potential of the bath was found to be 1.09 volts.

Antimony: 1.16 g. of antimony oxychloride was used. Electrolysis at low current density gave a gray deposit in which small bright crystals were present. At higher current densities the deposit was a dark gray, loose powder. The deposition potential was found to be 0.95 volt and the decomposition potential 1.09 volts.

Izbekov and Chovnik (4) reported the decomposition potentials of solutions of antimony trichloride in a fused aluminum chloride and potassium chloride bath to be 0.85 volt at 250°C. and 0.82 volt at 350°C.

Bismuth: 1 mole per cent solutions were prepared by adding 1.56 g. of bismuth sesquioxide or 1.74 g. of bismuth oxychloride to the bath. On electrolysis at low current densities no metallic bismuth was deposited, but if the cathode was placed in 95 per cent ethyl alcohol to remove the melt, a reddish brown compound was found. It had a low melting point. When the cathode was placed in water, the compound apparently underwent autoöxidation and reduction to form a fine black deposit of free bismuth. The reddish brown deposit was formed at a potential of 1.11 to 1.08 volts, which is assumed to represent the reduction potential of trivalent bismuth to a lower valent form, probably bivalent.

By raising the current density metallic bismuth was obtained, but the values for the deposition potential were not consistent, probably because of varying concentrations of the reduced form of bismuth at the cathode surface. The probable value is 0.51 volt. The decomposition potentials are 1.01 volts and 1.62 volts, respectively, for the reduction and deposition reactions.

According to Weber (12) and to Deherain (2), chlorine reacts slowly with bismuth at room temperature, forming bismuth bichloride, a brown oily liquid.

Izbekov and Chovnik (4) obtained 0.64 volt for the decomposition potential of bismuth trichloride dissolved in a melt of aluminum chloride or of aluminum and potassium chlorides at 250°C. Izbekov and Skobets (5) found that the decomposition potential of bismuth trichloride dissolved in stannous chloride was 0.18 volt at 300°C.

Vanadium: 1.45 g. of potassium vanadyl fluoride was added to a bath that contained 1.00 g. less potassium chloride than the usual bath. In another series vanadium pentoxide was used. Because of the low volatility of the halides of vanadium, *n*-butyl alcohol was used in the vapor thermostat to maintain the temperature at 117°C.

At low current densities, the aluminum reference electrode *versus* cathode readings gave values of −0.11 volt when potassium vanadyl fluoride was used and −0.10 volt when vanadium pentoxide was used. At higher current densities the value obtained with the pentoxide solution was −0.04 volt.

The decomposition potential of the bath at lower current densities was 2.20 volts with potassium vanadyl fluoride and 2.19 volts with vanadium pentoxide.

A small amount of vanadium metal was identified on the cathode, but its deposition potential is as high as that of aluminum.

Marshall (8), using essentially the same procedure as the authors, found the deposition potential, as measured against an aluminum reference electrode, to be 0.00 volt and the decomposition potential of the bath to be 2.20 volts.

Columbium: 2.02 g. of potassium fluocolumbate or 0.89 g. of columbium pentoxide was added to the bath. Solution was slow, but at the end of 48 hr. all but a small amount had dissolved.

Electrolysis yielded a dark brown deposit that would drop off when introduced into ethyl alcohol, leaving a dark grey deposit which was insoluble in cold concentrated hydrochloric acid but soluble in hot. Its identity as metal or as a compound containing columbium at a lower valence was not determined.

The deposition potential of the bath was found to be 0.02 volt for the fluocolumbate and 0.03 volt for the pentoxide at low current densities. At high current densities the value was 0.00 volt.

Columbium is not deposited at a lower potential than aluminum.

Marshall (8) obtained values of 0.00 volt for the deposition potential and 2.10 volts for the decomposition potential of columbium solutions by the same procedure as the authors.

Tantalum: 2.62 g. of potassium fluotantalate or 1.42 g. of tantalum pentoxide was used. The former compound is more soluble. Upon electrolysis a loosely adherent, black deposit was formed. When the deposit was washed with ethyl alcohol, a grey adherent plate was exposed. Aluminum was removed by washing with hydrochloric acid, leaving a residue which dissolved in hot concentrated sulfuric acid.

The deposition potential was found to be −0.02 volt. At very low current densities, there was a straight portion of the curve which extrapolated to 0.84 volt. This is apparently the reduction potential of pentavalent tantalum to a lower valence state. The decomposition potential of the bath is about 2.08 volts at low current densities and 2.17 volts at higher.

Kirk and Bradt (6) reported 1.47 volts as the decomposition potential of a bath containing potassium fluotantalate and potassium chloride at 800°C.

Marshall (8) found the deposition potential to be 0.00 volt and the decomposition potential to be 2.10 volts.

Tellurium: 1.06 g. of tellurium dioxide was used. The bath was colored an intense purple. Electrolysis at low current densities produced no deposit, but when the data were plotted a straight line was obtained, extrapolating to 1.47 volts. At higher current densities a loose black deposit appeared at a potential of 1.07 volts. The decomposition potential at low current densities is 0.60 volt. The curves representing data for higher current densities were irregular.

TABLE 2

ELEMENT	I DEPOSITION POTENTIAL	II DECOMPOSITION POTENTIAL	SUM OF I AND II
Vanadium Manganese Titanium Tantalum Germanium Columbium	Not deposited at lower potentials than aluminum		
Chromium	0.16	1.95	2.11
Gallium	0.20 (approx.)	2.0 (approx.)	
Zinc	0.24	1.82	2.06
Molybdenum	0.31	1.87	2.18
Cadmium	0.36	1.74	2.10
Lead	0.36	1.74	2.10
Tungsten	0.39	1.68	2.07
Iron	0.47	1.58	2.05
Tin	0.49	1.62	2.11
Bismuth	0.51	1.62	2.13
Copper	0.62	1.46	2.08
Silver	0.66	1.41	2.07
Cobalt	0.69	1.49	2.18
Nickel	0.80	1.25	2.05
Mercury	0.91	1.16	2.07
Antimony	0.95	1.09	2.04
Arsenic	1.00	1.09	2.09
Hydrogen	1.05	1.03	2.08
Tellurium	1.07		

The value of 1.47 volts represents a reduction potential. Since no product of electrolysis adhered to the cathode, it was soluble in the bath. At higher current densities, the irregularities in the curves may be attributed to changes in cathodic surface area as metallic tellurium was being deposited.

A considerable amount of metallic tellurium was prepared by electrolyzing for several hours at 10 volts. The bath was extracted with water, leaving intensely black needles of metallic tellurium.

DISCUSSION

The metals whose deposition potentials have been determined in 1 mole per cent solutions in the aluminum chloride–sodium chloride–potassium chloride melt are given in table 2.

The cell formed by the aluminum reference electrode and the cathode upon which the metal, M, is deposited may be represented as follows:

$$\mathrm{Al} \mid \mathrm{AlCl_3}\ (\mathrm{NaCl, KCl}) \,\vdots\vdots\, \mathrm{AlCl_3}\ (\mathrm{NaCl, KCl}),\ \mathrm{MCl}_n \mid \mathrm{M}$$

where MCl_n is the chloride of the metal of valence n. The deposition potentials represent the electrode potentials of the metal in a 1 mole per cent solution as referred to the electrode potential of aluminum in a 66 mole per cent solution.

It was found that most of the deposition potentials of the metals measured were reproducible to within ± 0.02 volt.

The cell formed by the cathode and the anode may be represented as follows:

$$\mathrm{M} \mid \mathrm{MCl}_n\ (\mathrm{AlCl_3, NaCl, KCl}) \mid \mathrm{Cl_2}$$

The measured potentials represent the decomposition potentials of a 1 mole per cent solution of the substance MCl_n.

The numerical sum of the deposition potential and of the decomposition potential should equal the potential of the cell

$$\mathrm{Al} \mid \mathrm{AlCl_3}\ (\mathrm{NaCl, KCl}) \mid \mathrm{Cl_2}$$

which was found to be 2.07 volts in a previous study. The experimental values are given in column III and it is assumed that the fairly good agreement with the theory indicates the accuracy of the experimental data.

The series obtained in this study does not conform to the familiar series in a water system. Hydrogen is the most noble element, except for tellurium. Lead, bismuth, copper, and silver are comparatively less noble than cobalt and nickel. The divergences between the aluminum chloride–alkali chloride system and the water system are probably related to differences in solvation of the metal ions and in degrees of association of the solutes.

REFERENCES

(1) Coerver: Thesis, St. Louis University, 1941.
(2) Deherain: Bull. soc. chim. [1] **3,** 51 (1861).
(3) Drossbach: Z. Elektrochem. **44,** 288 (1938).
(4) Izbekov and Chovnik: Mem. Inst. Chem. Acad. Sci. Ukrain. S. S. R. **4,** 57 (1937).
(5) Izbekov and Skobets: Mem. Inst. Chem. Acad. Sci. Ukrain. S. S. R. **4,** 85 (1937).
(6) Kirk and Bradt: Trans. Electrochem. Soc. **70,** 231 (1936).
(7) Lorenz and Velde: Z. anorg. allgem. Chem. **183,** 81 (1929).
(8) Marshall: Dissertation, St. Louis University, 1942.
(9) Marshall and Yntema: J. Phys. Chem. **46,** 353 (1942).
(10) Skobets and Abarbarchuk: Mem. Inst. Chem. Acad. Sci. Ukrain. S. S. R., **6,** 71 (1939).
(11) Verdieck and Yntema: J. Phys. Chem. **46,** 344 (1942).
(12) Weber: Pogg. Ann. **96,** 130, 496 (1855).