Application Bulletin 36/2 e

Metrohm

Polarographic Analyses
Half wave potentials of metal ions

Of interest to:
General analytical chemistry
B 1

Summary

In the following tables the half-wave potentials or peak potentials of 90 metal ions are listed. The half-wave potentials (listed in Volt) are measured at the dropping mercury electrode (DME) at 25°C unless indicated otherwise.

Electrodes

WE	MME	6.1246.020
AE	Pt *or* Glassy Carbon	6.0343.000 6.1241.020 + 6.1247.000
RE	Ag/AgCl/KCl (3 mol/L)	6.0728.020 6.1245.010

In some cases other electrodes are specified.

Legend

w	Well marked wave or peak
i	Poor wave or evaluation impossible (e.g. in the region of increasing background current of the supporting electrolyte)
cw	Catalytic reduction of hydrogen (in some cases suitable for quantitative analysis)
NR	No signal of the respective metal ion (polarographic or voltammetric analysis not possible)
↓	Formation of precipitate. Attention to solubility product!
–	No information available

Part 1: Various metals and transition metals

Electrolytes

Acetate	c(CH_3COOH) = 2 mol/L + c(CH_3COONH_4) = 2 mol/L pH 4.6
NH_3 / NH_4Cl	c(NH_3) = 1 mol/L + c(NH_4Cl) = 1 mol/L pH 9.6
KCl	c(KCl) = 1 mol/L
HCl	c(HCl) = 1 mol/L
NaOH	c(NaOH) = 1 mol/L
KNO_3	c(KNO_3) = 0.1 mol/L
KSCN	c(KSCN) = 1 mol/L
TEA	c(Triethanolamine) = 0.3 mol/L + c(KOH) = 0.1 mol/L
Tartrate	c(Na_2-tartrate) = 0.5 mol/L pH = 9.0
Na_2EDTA	c(Na_2EDTA) = 0.1 mol/L
Citrate	c(Na_3-citrate) = 0.1 mol/L + c(NaOH) = 0.1 mol/L
Oxalate pH 2	c(Ammonium oxalate) = 0.1 mol/L, pH setting with H_2SO_4
Oxalate pH 4	c(Ammonium oxalate) = 0.1 mol/L, pH setting with H_2SO_4
Oxalate pH 6	c(Ammonium oxalate) = 0.1 mol/L, pH setting with H_2SO_4
Oxalate pH 8	c(Ammonium oxalate) = 0.1 mol/L, pH setting with NH_3

Metal Ion	Acetate	NH_3/NH_4Cl	KCl	HCl	NaOH	KNO_3	KSCN	TEA	Tartrate	Na_2EDTA	Citrate	Oxalate pH 2	Oxalate pH 4	Oxalate pH 6	Oxalate pH 8
Al(III)	NR	NR	–1.59 i	NR	NR	NR	NR	NR	NR	NR	NR	–	–	–	–
As(III)	–0.95	–1.62 i	–0.07 i	–0.38 w –0.62	–0.25	–0.11 w	NR	–0.16	NR	–1.23 w	–0.22 w	NR	–1.56 w	–1.70 i	–1.58 i
Bi(III)	–0.21 w	NR	–0.06 w	–0.07 w	–0.68	–1.17 i ↓	NR	–0.87 w	–0.31 w cw	–0.54 w	–0.77 w	–0.13 w	–0.21 w	–0.22 w	–0.26 w ↓
Cd(II)	–0.63 w	–0.77 w	–0.62 w	–0.61 w	–0.82 i	–0.55 w	–0.62 w	–0.81	–0.64	NR cw	–0.68 i	–0.56 w	–0.61 w	–0.62 w	–0.62 w
Ce(IV)	NR	NR	NR	NR	NR	NR ↓	NR	NR	NR	NR	NR	–	–	–	–
Co(II)	NR	–1.26	–1.38	NR	NR ↓	–1.27 w –1.54	–1.11	NR	–1.53	NR	NR	NR	NR	NR	–1.52 i
Cr(III)	–1.20 i	–1.34 w ↓	–1.03	–1.00 w	NR ↓	–0.87 –1.01	–1.01 w	NR	–1.58 i	–1.20 w	NR	NR	NR	–1.73 i	NR
Cr(VI)	NR	–0.28 w –1.45 w –1.68	–0.38 –0.88 w	–1.03 i	–0.85 w	–0.32 –1.10	–0.41 –1.00 w	–1.27 w	–0.33 –0.86 –1.71	–1.20 w	–0.73 w	NR	NR	–0.02 w	–1.14 w –1.72 i
Cu(II)	–0.25 w	–0.20 w –0.46 w	–0.18	–0.20	–0.35 –0.43	NR	–0.64	–0.50	–0.08 w	–0.26 w	–0.41 w	–0.05 w	–0.15 w	–0.18 w	–0.18 w
Fe(II)	NR	–1.44 w	–1.57 i cw	i cw	–1.55 i ↓	–1.31 –1.56 i cw	–1.59 w	–1.02 w –1.68	–1.51 i	–0.09 w	–0.83 w –1.57 w	–0.02 w	–0.17	–0.18 w	–0.18 w –1.61 i
Fe(III)	–0.02 –0.24	NR ↓	–1.42 i	NR	NR ↓	–1.29 i	–1.56 w	–0.99 w –1.68	–0.19 –1.53 w	–0.11 w	–0.85 w –1.59 w	–0.18 w	–0.17 w	–0.19 w	–0.19 w
Ge(IV)	–1.34 i	–1.41	NR	NR	NR	–1.26 i cw	i cw	NR	NR	NR	NR	NR	NR	–1.38 w	–1.38 w
In(III)	–0.67 w	–1.08	–0.57	–0.57	–1.12 w	–0.90 i	–0.59 w	–1.51 w	NR	NR	–1.17	–0.61 w	–0.67 w –0.84 w	–0.68 w –0.87 w	–0.70 w –1.18
Mn(II)	NR	–1.59 w	–1.55 w	NR	–1.68 i ↓	–1.46 i	–1.56 i	–0.44 –1.66 i	–1.52 w	NR	NR	NR	NR	–1.61 i	–1.60 i

Metal Ion	Acetate	NH_3/NH_4Cl	KCl	HCl	NaOH	KNO_3	KSCN	TEA	Tartrate	Na_2EDTA	Citrate	Oxalate pH 2	Oxalate pH 4	Oxalate pH 6	Oxalate pH 8
Mo(VI)	–0.63 w –1.15 –1.30	NR	NR	–0.08 i	NR	NR	NR	NR	NR	–0.52 –0.75 w	NR	–0.02 –0.11 –0.33 w –0.74 w	–0.17 w –0.29 –0.59	NR	NR
Ni(II)	–1.09 w	–1.07 w	–1.03	NR	NR ↓	–1.00 w	–0.66 w	–1.36	NR	NR	NR	NR	NR	NR	–1.32
Pb(II)	–0.47 w	–0.47 w	–0.41 w	–0.41 w	–0.73 ↓	–0.36 w	–0.39 w	–0.91	–0.59	–1.03 w	–0.69 w	–0.40 w	–0.45 w	–0.56 w	–0.57 w
Pd(II)	–0.53 –0.76	–0.75 w	i cw	NR	–1.33 i	NR	i cw	–1.01 i ↓	NR	NR	NR	–	–	–	–
Sb(III)	–0.39 –0.50 w	–0.81 w	–0.07 –0.15 w	–0.12 w	–0.42 –1.18	–0.19 w	–0.58 w –0.70	–1.31 w	NR	–0.64 w	–0.33 –0.95 w	–0.33 w	–0.46 w	–0.41 w –0.57 w	–0.76 w
Se(IV)	–0.70 w –1.19	–1.54 w	NR	–0.06 –0.47	NR	NR	NR	NR	–1.21	–0.67 w –1.20 w	NR	–0.03 –0.60 w	–0.68 w –1.11	–1.35	–1.35
Sn(II)	–0.13 w –0.63 w	–0.72	–0.43 w	–0.45 w	–0.83 –1.15 w	–0.35 w	–0.45 w –1.59 w	–0.75 w –1.15 w	–0.54 –0.83 –1.06	–0.13	–0.83 w –1.08 w	–0.12 w –0.51 w	–0.15 w –0.62 w	–0.26 w –0.62 w	–0.51 i –0.64 i
Sn(IV)	NR	NR	NR ↓	–0.45	NR ↓	NR	–1.57	NR	NR	–1.16 i	NR	–0.51 w	NR	NR	NR
Ti(III)	–	–	–	–	–	–	–	–	–	–	–	–0.31 w	–0.41 w	–0.52	–0.70
Ti(IV)	–	–	–	–	–	–	–	–	–	–	–	–0.29	–0.42	NR	NR ↓
Tl(I)	–0.44 w	–0.46 w	–0.47	–0.46 w	–0.45	–0.43 w	–0.50 w	–0.45 w	–0.45 w	–0.44 w	–0.47 w	–0.44	–0.44	–0.44	–0.44
U(VI)	–0.42 w	NR	–0.18 i	–0.17	–0.92 i	NR	NR	–0.87	NR	NR	NR	–0.18 w	–0.32	–0.38 w	–0.42 w
V(V)	i cw	–1.12 –1.29 i	–1.10 i cw	–1.11 i	–0.40 i	–1.03 i	–0.50 w	–0.35	–0.33 i	–1.23	–0.76 –1.11 w	NR	NR	–0.90 –1.30 w	–0.19 w –0.88 –1.29 w
W(VI)	–0.26 i	NR	NR	–1.01 i cw	NR	NR	NR	NR	NR	–1.26 i	NR	–	–	–	–
Zn(II)	–1.05	–1.32 w	–0.99 w	–0.99 i	–1.58	–0.97	–1.01 w	–1.58	–1.27 w	NR	–1.38 w	NR	NR	–1.38	–1.29
Zr(IV)	NR	NR	–1.49 w	NR	NR	–0.95 w	–1.58 w	NR	NR cw	NR	NR	–	–	–	–

Part 2: Alkaline and alkaline earth metals

Electrolytes

c(TEAI) = 0.1 mol/L	c(tetraethylammonium iodide) = 0.1 mol/L in water
c(TEAI) = 0.1 mol/L, 20% DMF	c(tetraethylammonium iodide) = 0.1 mol/L in water:dimethylformamide 80:20

Half-wave potentials

Metal Ion	Supporting electrolyte	Half-wave potential
Ba(II)	c(TEAI) = 0.1 mol/L	–1.90
Be(II)	c(TEAI) = 0.1 mol/L, pH 2.3	–1.91
Ca(II)	c(TEAI) = 0.1 mol/L	–2.24 i
Cs(I)	c(TEAI) = 0.1 mol/L	–2.04
K(I)	c(TEAI) = 0.1 mol/L	–2.11
Li(I)	c(TEAI) = 0.1 mol/L	–2.31
Mg(II) [1]	c(TEAI) = 0.1 mol/L	[2]
Na(I)	c(TEAI) = 0.1 mol/L	–2.07
Rb(I)	c(TEAI) = 0.1 mol/L	–2.06
Sr(II)	c(TEAI) = 0.1 mol/L, 20% DMF	–1.85

Remarks

Alkaline and alkaline earth metals usually cannot be determined in real samples because the signals are not well separated from each other.

[1] Magnesium is determined indirectly as an oxime or as a complex with solochrome violet RS.

[2] Maximum, non exploitable.

Part 3: Rare-earth elements

Electrolytes

c(TEA-ClO_4) = 0.1 mol/L in DMF	c(tetraethylammonium perchlorate) = 0.1 mol/L in dimethylformamide

Half-wave potentials

Metal Ion	Supporting electrolyte	Half-wave potential [3]
Ce	c(TEA-ClO_4) = 0.1 mol/L in DMF	–2.44
Dy	c(TEA-ClO_4) = 0.1 mol/L in DMF	–2.08
Er	c(TEA-ClO_4) = 0.1 mol/L in DMF	–2.16
Eu	c(TEA-ClO_4) = 0.1 mol/L in DMF	–0.80 –2.30
Gd	c(TEA-ClO_4) = 0.1 mol/L in DMF	–2.12
Ho	c(TEA-ClO_4) = 0.1 mol/L in DMF	–2.20
La	c(TEA-ClO_4) = 0.1 mol/L in DMF	–2.16
Lu	c(TEA-ClO_4) = 0.1 mol/L in DMF	–2.08
Nd	c(TEA-ClO_4) = 0.1 mol/L in DMF	–2.22
Pm	c(TEA-ClO_4) = 0.1 mol/L in DMF	– (radioactive)
Pr	c(TEA-ClO_4) = 0.1 mol/L in DMF	–2.24
Sm	c(TEA-ClO_4) = 0.1 mol/L in DMF	–1.98
Sc	c(TEA-ClO_4) = 0.1 mol/L in DMF	–1.76
Tb	c(TEA-ClO_4) = 0.1 mol/L in DMF	–2.16
Tm	c(TEA-ClO_4) = 0.1 mol/L in DMF	–2.10
Yb	c(TEA-ClO_4) = 0.1 mol/L in DMF	–1.58
Y	c(TEA-ClO_4) = 0.1 mol/L in DMF	–2.06

Remarks

For preparation of the standard solutions the oxides of the rare-earth elements are first dissolved in aqua regia, dried in a vacuum desiccator, and then dissolved in DMF.

With the exception of Ce, Sc, and Yb, the half-wave potentials of all metals become more positive with increasing concentrations.

[3] The reference electrode is filled with supporting electrolyte.

Part 4: Actinides and technetium

Electrolytes

c($LiClO_4$) = 0.1 mol/L, pH 1.9 ... 3.1	c($LiClO_4$) = 0.1 mol/L in water. The pH value is adjusted to 1.9 ... 3.1.
c(KCl) = 0.5 mol/L, pH 2	c(KCl) = 0.5 mol/L in water. The pH value is adjusted to 2.

Half-wave potentials

Metal Ion	Supporting electrolyte	Half-wave potential	Literature
Ac	c($LiClO_4$) = 0.1 mol/L, pH 1.9 ... 3.1	–1.61	[1]
Am			[2]
Cf			[2]
Cm			[2]
Fm			[3]
Np			[4]
Pu	$Al_2(SO_4)_3$ / citric acid, pH 4.5	–0.43	[5]
Tc	c(KCl) = 0.5 mol/L, pH 2	–0.15	[6]

Remarks

Since all these elements are highly radioactive, it was not possible to determine them in our laboratory. The following literature references are useful.

Literature

[1] F. David
Polarographie von Actinium
C.R. Acad. Sci. (Paris) Ser. C 271 (1970), 440-442
Ref.: Z.Anal.Chem. 256 (1971), 307

[2] F. David
Polarography of radioisotopes 115Eu, 169Yb, 153Gd, 241Am, 244Cm, 252Cf
Compt. Rend. 270 C (1970), 2112-2115
Ref.: Electroanal. Abstr. 9 (1971), 140

[3] F. David; M. Nussonois
Reduction of Fm(II) in acetic solution by electrolysis at controlled electric tension
Radiochem. Radioanal. Lett. 11 (1972), 1-5
Ref.: Electroanal. Abstr. 11 (1973), 328

[4] V.F. Peretruhin; D.P. Alekseeva
Polarographic behaviour of Np(VII) in alkaline aqueous solutions
Izv. Akad. Nauk. SSSR, Ser. Khim. 23 (1974), 1438
Ref.: Electroanal. Abstr. 13 (1975), 45

[5] G.W.C. Milner; A.J. Wood
The determination of plutonium by A.C. polarography
J. Electroanal. Chem. 7 (1964), 190-205
Ref.: Z. Anal. Chem. 219 (1965), 70

[6] G.B.S. Salaria; C.L. Rulfs; P.J. Elving
Polarographic and coulometric determination of technetium
Anal. Chem. 35 (1963), 979-982
Ref.: Z. Anal. Chem. 219 (1965), 440

Part 5: Miscellaneous

Electrolytes

c(TBAI) = 0.1 mol/L in 80% ethanol	c(tetrabutylammonium iodide) = 0.1 mol/L in water:ethanol 80:20
c(HCl) = 0.1 mol/L	c(HCl) = 0.1 mol/L in water.
c(KSCN) = 0.1 mol/L, pH 3	c(KSCN) = 0.1 mol/L in water. The pH value is adjusted to 3
c(NaOH) = 2 mol/L	c(NaOH) = 2 mol/L in water.
HCl conc.	w(HCl) = 32%
$Ca(OH)_2$ sat.	Saturated solution of $Ca(OH)_2$ in water.
$c(KNO_3)$ = 0.3 mol/L	$c(KNO_3)$ = 0.3 mol/L in water.
$c(H_2SO_4)$ = 0.1 mol/L	$c(H_2SO_4)$ = 0.1 mol/L in water.
$c(Na_2$-NTA) = 0.1 mol/L	c(nitrilotriacetate disodium salt) = 0.1 mol/L in water.
c(NaOH) = 0.1 mol/L / $c(KNO_3)$ = 0.1 mol/L	c(NaOH) = 0.1 mol/L + $c(KNO_3)$ = 0.1 mol/L in water.
c(EDTA) = 0.1 mol/L	c(ethylenediaminetetraacetic acid) = 0.1 mol/L in water.
c(TEA-ClO_4) = 0.1 mol/L in DMF	c(tetraethylammonium perchlorate) = 0.1 mol/L in dimethylformamide.

Metal Ion	Supporting electrolyte	Half-wave potential
Al(III)	c(TBAI) = 0.1 mol/L in 80% ethanol	–1.67
Au(III)	c(HCl) = 0.1 mol/L	+0.90 [4]
Ga(III)	c(KSCN) = 0.1 mol/L, pH 3	–0.84
Hf		NR
Ir(IV)	c(NaOH) = 2 mol/L	+0.38 [5]
Nb(V)	HCl conc.	–0.60
Os(VIII)	$Ca(OH)_2$ sat.	–0.42
Pt(IV)	$c(KNO_3)$ = 0.3 mol/L	–0.93 [6]
Re(VII)	$c(H_2SO_4)$ = 0.1 mol/L	–0.66
Rh(III)	$c(Na_2$-NTA) = 0.1 mol/L	–0.46
Ru(I)	c(NaOH) = 0.1 mol/L / $c(KNO_3)$ = 0.1 mol/L	–0.81 w [7]
Ta		NR
Ti(IV)	c(EDTA) = 0.1 mol/L	–0.34
Th(III)	c(TEA-ClO_4) = 0.1 mol/L in DMF	–1.46 –1.71

[4] With glassy carbon working electrode.

[5] With platinum working electrode.

[6] Negative peaks.

[7] With respect to the $Hg/Hg_2Cl_2/KNO_3$ sat. reference electrode.