Metrohm

Application Bulletin 36/3 e

Half wave potentials of metal ions for the determination by polarography

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.

Instruments

VA instrument capable of operating a Multi-Mode Electrode and supporting differential pulse (DP) measuring mode

Electrodes

WE	Multi-Mode Electrode pro Unsilanized mercury drop capillary	6.1246.120 6.1226.030
RE	Ag/AgCl reference electrode Ag/AgCl/KCl (3 mol/L) Electrolyte vessel Filled with c(KCl) = 3 mol/L	6.0728.x20 6.1245.010
AE	Separate Pt rod electrode or Glassy carbon rod with Electrode holder	6.0343.x00 6.1247.000 6.1241.x20

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	–1.52 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	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

Comments

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

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	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

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

2 Maximum, non exploitable.

3 The reference electrode is filled with supporting electrolyte.

Comments

- 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.

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.
$Al_2(SO_4)_3$ / citric acid, pH 4.5	c($Al_2(SO_4)_3$) = 0.2 mol/L, c(citric acid) = 1 mol/L in water. The pH value is adjusted to 4.5.
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	Electrolyte	Half-wave potential	Reference
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)

Comments

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

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(6) G.B.S. Salaria; C.L. Rulfs; P.J. Elving
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Part 5: Miscellaneous

Electrolytes

c(TBAI) = 0.1 mol/L in 80% ethanol	c(tetrabutylammonium iodide) = 0.1 mol/L in water:ethanol 20:80
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.
$c(Na_2\text{-NTA})$ = 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.
$c(TEA\text{-}ClO_4)$ = 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
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)	$c(Na_2\text{-NTA})$ = 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)	$c(TEA\text{-}ClO_4)$ = 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.