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Thermodynamic Functions of Transfer of Single Ions from Water to Nonaqueous and Mixed Solvents

PART 3: STANDARD POTENTIALS OF SELECTED ELECTRODES

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Thermodynamic functions of transfer of single ions from water to nonaqueous and mixed solvents: Part 3—Standard potentials of selected electrodes

Abstract – Standard electrode potentials at 298.15 K and their temperature coefficients are reported for the hydrogen and eight metal-ion/metal electrodes and six anion, silver salt/silver electrodes in twenty solvents. They have been calculated from the standard molar Gibbs energy and entropy of transfer of the relevant ions from water into these solvents.

INTRODUCTION

The standard molar Gibbs free energies of transfer, $\Delta G_t^0(X^{\pm z}, W \rightarrow S)$, where $X^{\pm z}$ is a cation or anion with z charges, transferring from water W to solvent S have been compiled from the literature (ref. 1). They have served for the selection of a set of recommended or tentative ΔG_t^0 values for many solvents S and ions $X^{\pm z}$. These can serve as the basis for a set of electrode potentials for selected electrodes in non-aqueous solvents. These electrodes should relate to a cation and the corresponding metal or to an anion and the corresponding insoluble silver salt and silver metal. The data that are available for such cations as $(CH_3)_4N^+$ or such anions as ClO_4^- cannot be converted to electrode potentials on this basis.

The conversion from standard molar Gibbs free energies of transfer of the ions to the electrode potentials is made according to:

$$E_+^0(\text{non-aq}) = E_+^0(\text{aq}) + \Delta G_t^0/z_+ F$$

for cations, and the corresponding equation:

$$E_-^0(\text{non-aq}) = E_-^0(\text{aq}) - \Delta G_t^0/z_- F$$

for anions. F is the Faraday constant and $z_\pm$ the number of electrons involved in the electrode reaction. Values of $E^0(\text{aq})^\pm$ have been calculated back from the standard molar Gibbs free energies of formation of the aqueous cation or anion involved, and of the silver salt corresponding to the anion, taken from ref. 2.

The temperature coefficients of the standard electrode potentials are obtained from the standard molar entropies of transfer and the temperature coefficient of the electrode potentials in aqueous solutions in a similar manner:

$$dE_\pm^0/dT(\text{non-aq}) = dE_\pm^0(\text{aq})/dT \mp \Delta S_t^0/z_\pm F$$

The values of ΔS_t^0 are taken from ref. 3.

The errors associated with the selected values of ΔG_t^0 for the ions involved have been estimated at ± 3 kJ mol^{-1}. This corresponds to ± 0.03 V in $E^0(\text{non-aq})$ on the basis that $E^0(\text{aq})$ is considerably more accurate. The values of $E^0(\text{non-aq})$ have therefore been given to two significant decimals. The errors associated with the selected values of ΔS_t^0 for the ions involved have been estimated at ± 6 JK^{-1} mol^{-1}. This corresponds to ± 0.06 mV/K in dE^0/dT so that the values of these coefficients are given to two significant decimals.

The E^o data are presented in Tables 1 and 2 for cation-responsive and anion-responsive electrodes, respectively. The dE^o/dT data are shown in Table 3. The abbreviations of the names of the non-aqueous solvents are listed below.

ABBREVIATIONS

MeOH	=	methanol
PrOH	=	1-propanol
En(OH)$_2$	=	1,2-ethanediol
PC	=	1,2-propanediol carbonate (propylene carbonate)
FA	=	formamide
DMA	=	N,N-dimethylacetamide
NMPy	=	N-methylpyrrolidinone
MeNO$_2$	=	nitromethane
DMSO	=	dimethyl sulfoxide
HMPT	=	N,N,N',N',N'',N''-hexamethyl phosphoric triamide
1,1DClE	=	1,1-dichloroethane
EtOH	=	ethanol
TFE	=	2,2,2-trifluoroethanol
Me$_2$CO	=	acetone
DMF	=	N,N-Dimethylformamide
DMThF	=	N,N-dimethyl thioformamide
MeCN	=	acetonitrile
PhNO$_2$	=	nitrobenzene
TMS	=	tetramethylene sulfone (sulfolane)
1,2DClE	=	1,2-dichloroethane

TABLE 1. Electrodes responsive to cations, standard potentials of elec-- trodes in non-aqueous solvents at 298.15 K against the aqueous standard hydrogen electrode (in V).

Electrode	$H^+/(1/2)H_2$	Li^+/Li	Na^+/Na	K^+/K	Rb^+/Rb	Cs^+/Cs	Ag^+/Ag	Tl^+/Tl	Cu^{2+}/Cu
Solvent:									
water	0.000	-3.040	-2.714	-2.936	-2.943	-3.027	0.799	-0.336	0.339
MeOH	0.10	-2.99	-2.63	-2.84	-2.84	-2.94	0.87	-0.29	0.47
EtOH	0.12	-2.93	-2.57	-2.77	-2.78	-2.87	0.85	-0.26	0.58
PrOH	0.09	-2.93	-2.54	-2.75	-2.75	-2.85	0.81		0.56
TFE				-2.53			1.32		
En(OH)$_2$	0.05	-3.04	-2.74	-2.96			0.81		
Me$_2$CO				-2.90	-2.90	-2.99	0.89		
PC	0.52	-2.79	-2.56	-2.88	-2.95	-3.10	0.99	-0.22	0.73
FA			-3.14	-2.80	-2.98	-3.00	-3.09	0.64	
DMF	-0.19	-3.14	-2.81	-3.04	-3.04	-3.14	0.58	-0.46	0.25
DMA			-2.84	-3.06	-3.03	-3.20	0.50		
DMThF		-2.47	-2.31	-2.66		-2.88	-0.26	-0.50	
NMPy	-0.26	-3.40	-2.87	-3.05	-3.03	-3.13	0.53	-0.49	
MeCN	0.48	-2.73	-2.56	-2.88	-2.88	-2.97	0.56	-0.25	0.65
MeNO$_2$			-2.54	-2.45	-2.74	-2.92	-3.02	1.02	
PhNO$_2$	0.34	-2.65	-2.54	-2.70	-2.75	-2.87		-0.18	
DMSO	-0.20	-3.20	-2.85	-3.07	-3.05	-3.16	0.44	-0.56	0.09
TMS			-2.75	-2.98	-3.04	-3.13	0.76		0.71
HMPT				-3.10			0.32		
1,1DClE			-2.41	-2.63	-2.64	-2.74			
1,2DClE			-2.46	-2.67	-2.68	-2.78			

TABLE 2.   Electrodes responsive to anions, standard potentials of elec-
trodes in non-aqueous solvents at 298.15 K against the aqueous
standard hydrogen electrode (in V).

Electrode:	Cl^-,AgCl/Ag	Br^-, AgBr/Ag	I^-,AgI/Ag	CN^-,AgCN/Ag	SCN^-, AgSCN/Ag	N_3^-,AgN$_3$/Ag
Solvent:						
water	0.222	0.073	−0.152	−0.161	0.090	0.290
MeOH	0.09	−0.04	−0.23	−0.25	0.03	0.20
EtOH	0.01	−0.12	−0.29	−0.23		0.12
PrOH	−0.05	−0.16	−0.35			
TFE	0.33	0.15	−0.07			
En(OH)$_2$	0.13	0.00	−0.18		0.04	0.22
Me$_2$CO	−0.37	−0.42	−0.41	−0.66		−0.15
PC	−0.19	−0.24	−0.29	−0.53	0.02	0.01
FA	0.08	−0.04	−0.23	−0.30	0.02	0.18
DMF	−0.28	−0.38	−0.36	−0.58	−0.10	−0.02
DMA	−0.34		−0.37		−0.13	−0.12
DMThF						
NMPy	−0.31	−0.31	−0.35		−0.10	−0.18
MeCN	−0.21	−0.25	−0.33	−0.52	−0.06	−0.09
MeNO$_2$	−0.16	−0.24	−0.33		−0.07	0.00
PhNO$_2$	−0.14	−0.23	−0.34			
DMSO	−0.20	−0.21	−0.26	−0.52	−0.01	0.02
TMS	−0.26	−0.29	−0.37		−0.14	−0.13
HMPT	−0.38	−0.41	−0.46		−0.12	−0.22
1,1DClE	−0.38	−0.37	−0.47			
1,2DClE	−0.38	−0.33	−0.42			

TABLE 3.   The temperature coefficients of standard electrode potentials
at 298.15 K (in mV/K).

Solvent:	Water	MeOH	EtOH	PrOH	PC	FA	DMF	MeCN	DMS
Electrode:									
Li$^+$/Li	−0.51	0.35	0.54	0.53	0.16	−0.64	−0.03		−0.06
Na$^+$/Na	−0.76	0.22	0.36	0.34	0.02	−0.46	−0.07	0.17	−0.18
K$^+$/K	−1.07	−0.10	0.10	0.18	−0.15	−0.65	−0.18	0.00	−0.24
Rb$^+$/Rb	−1.14	−0.26	−0.07	0.08	−0.34	−0.72	−0.29	−0.07	−0.24
Cs$^+$/Cs	−1.17	−0.38	−0.21	−0.09	−0.49	−0.78	−0.36	−0.13	−0.40
Ag$^+$/Ag	−0.99	−0.01			−0.04		−0.34	0.05	−0.07
Cl$^-$/AgCl,Ag	0.65	0.47	0.31	0.05	0.20	0.32	−0.38	−0.12	0.01
Br$^-$/AgBr,Ag	0.49	0.25	0.04	−0.18	−0.04	0.09	−0.61	−0.30	−0.35
I$^-$,AgI,Ag	0.28	−0.04	−0.20	−0.45	−0.38	−0.21	−0.95	−0.60	−0.61
N$_3$$^-$/AgN$_3$,Ag	0.20	−0.15			−0.24		−1.10	−0.55	−0.75

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