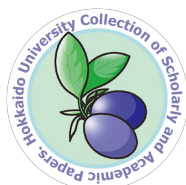




HOKKAIDO UNIVERSITY

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— Addendum —

STANDARD MOLAL REAL FREE ENERGIES
OF SOLVATION OF INDIVIDUAL IONS
AND ELECTROMOTIVE FORCES OF
SINGLE ELECTRODES IN NON-
AQUEOUS SOLUTIONS

— An Additional Remark —

By

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(Received May 30, 1980)

The values of the standard molal real free energies of solvation α_i^o 's of monoatomic ions in non-aqueous solvents at 25°C and those of the standard electromotive forces φ_i^o 's referred to the standard state of the gaseous electron at 25°C were estimated in the previous work¹⁾ by an empirical method which was developed on the basis of the standard electromotive forces referred to the standard hydrogen electrode.

In the present addendum article Table II in the previous work¹⁾ in which the values of α_i^o and φ_i^o for 17 ionic species were listed are supplemented by 54 ionic species for which we have no experimental data of the standard electromotive forces referred to a definite reference electrode in non-aqueous solvents. The values of α_i^o and φ_i^o for such ions are calculated by Eqs. (14) and (8)

$$z_i F(\varphi_i^o - \varphi_{i,aq}^o) = \alpha_i^o - \alpha_{i,aq}^o \cdots (14), \quad -\frac{1}{z_i} \alpha_i^o = \beta x, \cdots (8)$$

using the β -values in Table I in the previous work¹⁾ and $\alpha_{i,aq}^o$ -values reported in Ref. 2, and are listed in Tables I and II with the symbol # in the present article. For convenience Table II in the previous work are also repeated in these tables (for the symbols *) and **), see Ref. 1).

References

- 1) A. Matsuda, *J. Res. Inst. Catalysis, Hokkaido Univ.*, **27**, 101 (1979).
- 2) A. Matsuda, *J. Res. Inst. Catalysis, Hokkaido Univ.*, **27**, 167 (1979).

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TABLE I. Standard molal real free energies of solvation of individual ions $-\alpha_i^0/z_i$ in non-aqueous solvents at 25°C in electron volts

β M^z_i	H ₂ O	CH ₃ OH	C ₂ H ₅ OH	HCOOH	CH ₃ CN	HCONH ₂	N ₂ H ₄	DMSO	Quino- line
		0.994	1.001	0.957	0.974	1.011	1.108	0.995	1.066
H ⁺	11.30	11.22	11.30	10.60	11.04	11.39	12.63	11.20	12.08
Li ⁺	5.30	5.28	5.31	5.05	5.24	5.36*	5.80	5.15	5.65*
Na ⁺	4.26	4.19	4.20	4.27	4.16	4.31*	4.70	4.24*	4.54*
K ⁺	3.50	3.48*	3.50*	3.24	3.48	3.54	3.93	3.48*	3.73*
Rb ⁺	3.27	3.25*	3.27*	3.03	3.19	3.22	3.62	3.25*	3.49
Cs ⁺	2.94	2.92*	2.94*	2.66	2.82	2.97*	3.26*	2.93*	3.13*
Cu ⁺	5.91	5.87*	5.91	5.66*	5.79	5.98*	7.54	6.01	6.30*
Cu ²⁺	10.78	10.71	10.92	10.29	10.59	10.94	11.94*	10.70	11.45
Ag ⁺	4.94	4.93*	5.01	4.89	5.27	5.01*	6.32	4.98	5.29*
Au ⁺	6.29	6.25#	6.30#	6.02#	6.13#	6.36#	6.97#	6.26#	6.71#
Au ³⁺	14.83	14.74#	14.84#	14.19#	14.44#	14.99#	16.43#	14.76#	15.81#
Be ²⁺	12.53	12.45#	12.54#	11.99#	12.20#	12.67#	13.88#	12.47#	13.36#
Mg ²⁺	9.88	9.82#	9.89#	9.46#	9.62#	9.99#	10.95#	9.83#	10.53#
Ca ²⁺	8.26	8.21*	8.27*	7.89	7.88	8.35*	8.63	8.22*	8.81*
Sr ²⁺	7.53	7.48#	7.54#	7.21#	7.33#	7.61#	8.34#	7.49#	8.03#
Ba ²⁺	6.85	6.81#	6.86#	6.56#	6.67#	6.93#	7.59#	6.82#	7.30#
Ra ²⁺	6.71	6.67#	6.72#	6.42#	6.54#	6.78#	7.43#	6.68#	7.15#
Zn ²⁺	10.51	10.40	10.38	10.09	10.22	10.59	11.48	10.46*	11.20*
Cd ²⁺	9.34	9.28	9.31	8.98	9.14	9.43	10.36	9.29	9.96*
Hg ²⁺	9.48	9.42#	9.49#	9.07#	9.23#	9.58#	10.50#	9.43#	10.11#
Al ³⁺	15.95	15.85#	15.97#	15.26#	15.54#	16.13#	17.67#	15.87#	17.00#
Ga ²⁺	10.50	10.44#	10.51#	10.05#	10.23#	10.62#	11.63#	10.45#	11.19#
Ga ³⁺	15.99	15.89#	16.01#	15.30#	15.57#	16.17#	17.72#	15.91#	17.05#
In ⁺	3.71	3.69#	3.71#	3.55#	3.61#	3.75#	4.11#	3.69#	3.95#
In ³⁺	14.08	14.00#	14.09#	13.47#	13.71#	14.23#	15.60#	14.01#	15.01#
Tl ⁺	3.56	3.52	3.57	3.41*	3.47*	3.66	3.94*	3.48	3.79*
Tl ³⁺	14.17	14.08#	14.18#	13.56#	13.80#	14.33#	15.70#	14.10#	15.11#
Sc ³⁺	13.56	13.48#	13.57#	12.98#	13.21#	13.71#	15.02#	13.49#	14.45#
Y ³⁺	12.31	12.24#	12.32#	11.78#	11.99#	12.45#	13.64#	12.25#	13.12#
La ³⁺	11.14	11.07#	11.15#	10.66#	10.85#	11.26#	12.34#	11.08#	11.88#
Ce ³⁺	12.22	12.15#	12.23#	11.69#	11.49#	12.35#	13.54#	12.16#	13.03#
Ce ⁴⁺	16.88	16.78#	16.90#	16.15#	16.44#	17.07#	18.70#	16.80#	17.99#
Nd ³⁺	12.00	11.93#	12.01#	11.48#	11.69#	12.13#	13.30#	11.94#	12.79#
Sm ³⁺	12.25	12.18#	12.26#	11.72#	11.93#	12.38#	13.57#	12.19#	13.06#
Gd ³⁺	12.38	12.31#	12.39#	11.85#	12.06#	12.52#	13.72#	12.32#	13.20#
Lu ³⁺	13.10	13.02#	13.11#	12.45#	12.76#	13.24#	14.51#	13.03#	13.96#
Th ⁴⁺	16.70	16.60#	16.72#	15.98#	16.27#	16.88#	18.50#	16.62#	17.80#

Free Energies of Solvation of Ions and EMF of Single Electrodes

Table I. Continued

β	H ₂ O	CH ₃ OH	C ₂ H ₅ OH	HCOOH	CH ₃ CN	HCONH ₂	N ₂ H ₄	DMSO	Quino- line
M^{z_i}		0.994	1.001	0.957	0.974	1.011	1.108	0.995	1.066
U ³⁺	11.95	11.88#	11.96#	11.44#	11.64#	12.08#	13.24#	11.89#	12.74#
U ⁴⁺	17.23	17.13#	17.25#	16.49#	16.78#	17.42#	19.09#	17.14#	18.37#
Sn ²⁺	8.10	8.05#	8.11#	7.75#	7.89#	8.19#	8.97#	8.06#	8.63#
Pb ²⁺	7.76	7.75	7.78	7.65	7.49	7.85*	8.61	7.77	8.27*
Ti ²⁺	9.78	9.72#	9.79#	9.36#	9.53#	9.89#	10.84#	9.73#	10.43#
Zr ⁴⁺	18.14	18.03#	18.16#	17.36#	17.67#	18.34#	20.10#	18.05#	19.34#
Hf ⁴⁺	17.26	17.16#	17.28#	16.52#	16.81#	17.45#	19.12#	17.17#	18.40#
As ³⁺	15.36	15.21#	15.51#	14.70#	14.96#	15.53#	17.02#	15.28#	16.37#
Sb ³⁺	13.21	13.13#	13.22#	12.64#	12.87#	13.36#	14.64#	13.14#	14.08#
Bi ³⁺	12.49	12.42#	12.50#	11.95#	12.17#	12.63#	13.84#	12.43#	13.31#
V ²⁺	9.59	9.53#	9.60#	9.18#	9.34#	9.70#	10.63#	9.54#	10.22#
Nb ³⁺	15.31	15.22#	15.33#	14.65#	14.91#	15.48#	16.96#	15.23#	16.32#
Te ⁴⁺	20.19	20.07#	20.21#	19.32#	19.67#	20.41#	22.37#	20.09#	21.52#
Po ²⁺	9.28	9.22#	9.29#	8.88#	9.04#	9.38#	10.28#	9.23#	9.89#
Po ³⁺	13.69	13.61#	13.70#	13.10#	13.33#	13.84#	15.17#	13.62#	14.59#
Cr ²⁺	9.68	9.62#	9.69#	9.26#	9.43#	9.79#	10.73#	9.63#	10.32#
Cr ³⁺	15.02	14.93#	15.04#	14.37#	14.63#	15.19#	16.64#	14.94#	16.01#
F ⁻	-4.30	-4.27#	-4.30#						
Cl ⁻	-3.07	-2.91	-2.76	-3.32**	-2.55	-2.95**			
Br ⁻	-2.81	-2.71	-2.52		-2.47				
I ⁻	-2.48	-2.38	-2.25		-2.27				
Mn ²⁺	9.49	9.43#	9.50#	9.08#	9.24#	9.59#	10.51#	9.44#	10.12#
Fe ²⁺	9.84	9.78#	9.85#	9.42#	9.58#	9.95#	10.90#	9.79#	10.49#
Fe ³⁺	14.97	14.88#	14.98#	14.33#	14.58#	15.13#	16.59#	14.90#	15.96#
Ru ²⁺	10.06	10.00#	10.07#	9.63#	9.80#	10.17#	11.15#	10.01#	10.72#
Os ²⁺	10.24	10.18#	10.25#	9.80#	9.97#	10.35#	11.35#	10.19#	10.92#
Co ²⁺	10.49	10.43#	10.50#	10.04#	10.22#	10.61#	11.62#	10.44#	11.18#
Co ³⁺	16.25	16.15#	16.27#	15.55#	15.83#	16.43#	18.01#	16.17#	17.32#
Rh ³⁺	15.33	15.24#	15.35#	14.67#	14.93#	15.50#	16.99#	15.25#	16.34#
Ni ²⁺	10.74	10.63#	10.75#	10.28#	10.46#	10.86#	11.90#	10.69#	11.45#
Pd ²⁺	10.26	10.20#	10.27#	9.82#	9.99#	10.37#	11.37#	10.21#	10.94#
Pt ²⁺	10.46	10.40#	10.47#	10.01#	10.19#	10.58#	11.59#	10.41#	11.15#
e ⁻	-1.56	-1.55#	-1.56#	-1.49#	-1.52#	-1.58#	-1.73#	-1.55#	-1.66#
OH ⁻	-2.77	-2.75#	-2.77#	-2.65#	-2.70#	-2.80#	-3.07#	-2.76#	-2.95#

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TABLE II. Standard electromotive forces of single electrodes φ_i° in non-aqueous solutions at 25°C

Stn. El.	H ₂ O	CH ₃ OH	C ₂ H ₅ OH	HCOOH	CH ₃ CN	HCONH ₂	N ₂ H ₄	DMSO	Quino- line
H ⁺ / $\frac{1}{2}$ H ₂	4.42	4.50	4.42	5.12	4.68	4.33	3.09	4.52	3.64
Li ⁺ /Li	1.40	1.41	1.38	1.64	1.45	1.31*	0.89	1.53	1.02*
Na ⁺ /Na	1.71	1.78	1.76	1.70	1.81	1.66*	1.27	1.73*	1.43*
K ⁺ /K	1.50	1.51*	1.49*	1.76	1.52	1.46	1.07	1.51*	1.26*
Rb ⁺ /Rb	1.43	1.52*	1.50*	1.67	1.51	1.47	1.08	1.52*	1.21
Cs ⁺ /Cs	1.40	1.52*	1.50*	1.68	1.52	1.47*	1.18*	1.51*	1.31*
Cu ⁺ /Cu	4.94	4.98*	4.94	5.19*	5.06	4.87*	3.31	4.85	4.55*
Cu ²⁺ /Cu	4.77	4.84	4.63	5.26	4.96	4.61	3.64*	4.84	4.10
Ag ⁺ /Ag	5.22	5.26*	5.17	5.29	4.91	5.18*	3.86	5.20	4.90*
Au ⁺ /Au	6.12	6.16#	6.11#	6.39#	6.28#	6.05#	5.44#	6.15#	5.70#
Au ³⁺ /Au	5.92	6.01#	5.91#	6.56#	6.31#	5.76#	4.32#	5.99#	4.94#
Be ²⁺ /Be	2.72	2.80#	2.71#	3.26#	3.05#	2.58#	1.37#	2.78#	1.89#
Mg ²⁺ /Mg	2.08	2.14#	2.07#	2.50#	2.34#	1.97#	1.01#	2.13#	1.43#
Ca ²⁺ /Ca	1.55	1.62*	1.56*	1.92	1.93	1.48*	1.18	1.61*	1.02*
Sr ²⁺ /Sr	1.53	1.58#	1.52#	1.85#	1.73#	1.45#	0.72#	1.57#	1.03#
Ba ²⁺ /Ba	1.52	1.56#	1.51#	1.81#	1.70#	1.44#	0.78#	1.55#	1.07#
Ra ²⁺ /Ra	1.50	1.54#	1.49#	1.79#	1.67#	1.43#	0.78#	1.53#	1.06#
Zn ²⁺ /Zn	3.66	3.76	3.78	4.07	3.94	3.57	2.68	3.72*	2.98*
Cd ²⁺ /Cd	4.03	4.07	4.04	4.37	4.21	3.92	2.99	4.06	3.41*
Hg ²⁺ /Hg	5.27	5.33#	5.26#	5.68#	5.52#	5.17#	4.25#	5.32#	4.64#
Al ³⁺ /Al	2.75	2.85#	2.73#	3.44#	3.16#	2.57#	1.03#	2.83#	1.70#
Ga ²⁺ /Ga	3.97	4.03#	3.96#	4.42#	4.24#	3.85#	2.84#	4.02#	3.28#
Ga ³⁺ /Ga	3.90	4.00#	3.88#	4.59#	4.32#	3.72#	2.17#	3.98#	2.84#
In ⁺ /In	4.17	4.19#	4.17#	4.33#	4.27#	4.13#	3.77#	4.19#	3.93#
In ³⁺ /In	4.08	4.16#	4.07#	4.69#	4.45#	3.93#	2.56#	4.15#	3.15#
Tl ⁺ /Tl	4.08	4.12	4.08	4.23*	4.17*	3.99	3.70*	4.17	3.85*
Tl ³⁺ /Tl	5.13	5.22#	5.12#	5.74#	5.50#	4.97#	3.60#	5.20#	4.19#
Sc ³⁺ /Sc	2.34	2.42#	2.33#	2.92#	2.69#	2.19#	0.88#	2.41#	1.45#
Y ³⁺ /Y	2.05	2.12#	2.04#	2.58#	2.37#	1.91#	0.72#	2.11#	1.24#
La ³⁺ /La	2.05	2.12#	2.04#	2.53#	2.34#	1.93#	0.85#	2.11#	1.31#
Ce ³⁺ /Ce	1.94	2.01#	1.93#	2.47#	2.67#	1.81#	0.62#	2.00#	1.13#
Ce ⁴⁺ /Ce	2.96	3.06#	2.94#	3.69#	3.40#	2.77#	1.14#	3.04#	1.85#
Nd ³⁺ /Nd	1.98	2.05#	1.97#	2.50#	2.29#	1.85#	0.68#	2.04#	1.19#
Sm ³⁺ /Sm	2.01	2.08#	2.00#	2.54#	2.33#	1.88#	0.69#	2.07#	1.20#
Gd ³⁺ /Gd	2.02	2.09#	2.01#	2.55#	2.34#	1.88#	0.68#	2.08#	1.20#
Lu ³⁺ /Lu	2.19	2.27#	2.18#	2.84#	2.53#	2.05#	0.78#	2.26#	1.33#
Th ⁴⁺ /Th	2.52	2.62#	2.50#	3.24#	2.95#	2.34#	0.72#	2.60#	1.42#

Free Energies of Solvation of Ions and EMF of Single Electrodes

Table II. Continued

Stn. El.	H ₂ O	CH ₃ OH	C ₂ H ₅ OH	HCOOH	CH ₃ CN	HCONH ₂	N ₂ H ₄	DMSO	Quino- line
U ³⁺ /U	2.62	2.69#	2.61#	3.13#	2.93#	2.49#	1.33#	2.68#	1.83#
U ⁴⁺ /U	2.92	3.02#	2.90#	3.66#	3.37#	2.73#	1.06#	3.01#	1.78#
Sn ²⁺ /Sn	4.28	4.33#	4.27#	4.63#	4.49#	4.19#	3.41#	4.32#	3.75#
Pb ²⁺ /Pb	4.29	4.30	4.27	4.40	4.56	4.22*	3.44	4.28	3.80*
Ti ²⁺ /Ti	2.67	2.73#	2.66#	3.09#	2.92#	2.56#	1.61#	2.72#	2.02#
Zr ⁴⁺ /Zr	2.89	3.00#	2.87#	3.67#	3.36#	2.69#	0.93#	2.98#	1.69#
Hf ⁴⁺ /Hf	2.72	2.82#	2.70#	3.46#	3.17#	2.53#	0.86#	2.81#	1.58#
As ³⁺ /As	4.72	4.87#	4.57#	5.38#	5.12#	4.55#	3.06#	4.80#	3.71#
Sb ³⁺ /Sb	4.66	4.74#	4.65#	5.23#	5.00#	4.51#	3.23#	4.73#	3.79#
Bi ³⁺ /Bi	4.62	4.69#	4.61#	5.16#	4.94#	4.48#	3.27#	4.68#	3.80#
V ²⁺ /V	3.24	3.30#	3.23#	3.65#	3.49#	3.13#	2.20#	3.29#	2.61#
Nb ³⁺ /Nb	3.32	3.41#	3.30#	3.98#	3.72#	3.15#	1.67#	3.40#	2.31#
Te ⁴⁺ /Te	4.99	5.11#	4.97#	5.86#	5.51#	4.77#	2.81#	5.09#	3.66#
Po ²⁺ /Po	5.07	5.13#	5.06#	5.47#	5.31#	4.97#	4.07#	5.12#	4.46#
Po ³⁺ /Po	4.98	5.06#	4.97#	5.57#	5.34#	4.83#	3.50#	5.05#	4.08#
Cr ²⁺ /Cr	3.52	3.58#	3.51#	3.94#	3.77#	3.41#	2.47#	3.57#	2.88#
Cr ³⁺ /Cr	3.71	3.80#	3.69#	4.36#	4.10#	3.54#	2.09#	3.79#	2.72#
F ⁻ /½F ₂	7.07	7.04#	7.07#						
Cl ⁻ /½Cl ₂	5.78	5.62	5.47	5.97**	5.26	5.60**			
Br ⁻ /½Br ₂	5.49	5.39	5.20		5.15				
I ⁻ /½I ₂	4.95	4.86	4.73		4.75				
Mn ²⁺ /Mn	3.37	3.88#	3.81#	4.23#	4.07#	3.72#	2.80#	3.87#	3.19#
Fe ²⁺ /Fe	3.98	4.04#	3.97#	4.40#	4.24#	3.87#	2.92#	4.03#	3.70#
Fe ³⁺ /Fe	4.38	4.49#	4.39#	5.04#	4.79#	4.24#	2.78#	4.47#	3.41#
Ru ²⁺ /Ru	4.87	4.93#	4.86#	5.30#	5.13#	4.76#	3.78#	4.92#	4.21#
Os ²⁺ /Os	5.12	5.18#	5.11#	5.56#	5.39#	5.01#	4.01#	5.17#	4.44#
Co ²⁺ /Co	4.14	4.20#	4.13#	4.59#	4.41#	4.02#	3.01#	4.19#	3.45#
Co ³⁺ /Co	4.82	4.92#	4.80#	5.52#	5.24#	4.64#	3.06#	4.90#	3.75#
Rh ³⁺ /Rh	5.22	5.31#	5.20#	5.88#	5.62#	5.05#	3.56#	5.30#	4.21#
Ni ²⁺ /Ni	4.17	4.28#	4.16#	4.63#	4.45#	4.05#	3.01#	4.22#	3.46#
Pd ²⁺ /Pd	5.41	5.47#	5.40#	5.85#	5.68#	5.30#	4.30#	5.46#	4.73#
Pt ²⁺ /Pt	5.62	5.68#	5.61#	6.07#	5.89#	5.50#	4.49#	5.67#	4.93#
e _{aq} ⁻ /e _m ⁻	1.56	1.55#	1.56#	1.49#	1.52#	1.58#	1.73#	1.55#	1.66#
OH ⁻ /OH [•] _{aq}	6.42								