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—Short Note—

STANDARD MOLAL REAL FREE ENERGIES OF HYDRATION OF MONOATOMIC IONS AND STANDARD ELECTROMOTIVE FORCES OF SINGLE ELECTRODES IN AQUEOUS SOLUTIONS

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The standard electromotive force $E^{\circ}_{i,aq}$ of an electrochemical redox system M^{z_i}/M_i is conventionally referred to that of the hydrogen electrode. The standard electromotive force of the *single* hydrogen electrode $\phi^{\circ}_{H^+,aq}$ in aqueous solution was estimated in the previous work[1] to be 4.42 V at 25°C as referred to the standard state of the gaseous electron. The standard electromotive force $\phi^{\circ}_{i,aq}$ referred to the standard state of the gaseous electron can therefore be given by the equation

$$\phi^{\circ}_{i,aq} = E^{\circ}_{i,aq} + 4.42\ \mathrm{V}, \tag{1}$$

as discussed by Frumkin and Damaskin.[2]

On the other hand the standard molal real free energy of hydration $\alpha^{\circ}_{i,aq}$ of the ion $M_i^{z_i}$ is given in terms of $\phi^{\circ}_{i,aq}$ and ΔF°_i as

$$\Delta F^{\circ}_i = -\alpha^{\circ}_{i,aq} + z_i F \phi^{\circ}_{i,aq}, \tag{2}$$

where ΔF°_i is the molar free energy of formation of the ion $M^{z_i}_{i,g}$ and the electron in gaseous states from the element M_i (see Eq. (5) in ref. (1)). Since the value of ΔF°_i can be obtained from the thermochemical data (see below), it is possible to estimate $\alpha^{\circ}_{i,aq}$ on the basis of Eq. (2).

In the present work the values of $\alpha^{\circ}_{i,aq}$ and of $\phi^{\circ}_{i,aq}$ for monoatomic ions in solutions are estimated and summarized.

Estimation of ΔF°_i

ΔF°_i is given in terms of the electrochemical potentials of the ion $M^{z_i}_{i,g}$ in gaseous state, electron gas and the element M_i as

$$\Delta F^{\circ}_i = \bar{\mu}^{\circ}_{i,g} + z_i \bar{\mu}^{\circ}_{e,g} - \mu^{\circ}_{M_i}, \tag{3}$$

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TABLE Standard molal real free energies of hydration of monoatomic ions and standard electromotive forces of single electrodes in aqueous solutions

Single Electrode	$\Delta F^o/z$		H_2O		Single Electrode	$\Delta F^o/z$		H_2O	
	Th. Ch.	El. Ch.	$-\alpha^o/z$	ϕ^o		Th. Ch.	El. Ch.	$-\alpha^o/z$	ϕ^o
$H^+/\frac{1}{2}H_2$	15.72	15.72	11.30	4.42	Lu^{3+}/Lu	15.29		13.10	2.19
Li^+/Li	6.67	6.69	5.30	1.40	Th^{4+}/Th	19.22		16.70	2.52
Na^+/Na	5.97	5.97	4.26	1.71	U^{3+}/U	14.57		11.95	2.62
K^+/K	4.99	5.00	3.50	1.50	U^{4+}/U	20.15		17.23	2.92
Rb^+/Rb	4.77	4.70	3.27	1.43	Sn^{2+}/Sn	12.38		8.10	4.28
Cs^+/Cs	4.44	4.34	2.94	1.40	Pb^{2+}/Pb	12.07	12.05	7.76	4.29
Cu^+/Cu	10.85	10.85	5.91	4.94	Ti^{2+}/Ti	12.45		9.78	2.67
Cu^{2+}/Cu	15.58	15.55	10.78	4.77	Zr^{4+}/Zr	21.03		18.14	2.89
Ag^+/Ag	10.19	10.18	4.96	5.22	Hf^{4+}/Hf	19.98		17.26	2.72
Au^+/Au	12.41		6.29	6.12	As^{3+}/As	20.08		15.36	4.72
Au^{3+}/Au	20.75		14.83	5.92	Sb^{3+}/Sb	17.87		13.21	4.66
Be^{2+}/Be	15.25		12.53	2.72	Bi^{3+}/Bi	17.11		12.49	4.62
Mg^{2+}/Mg		11.96	9.88	2.08	V^{2+}/V	12.83		9.59	3.24
Ca^{2+}/Ca	9.83	9.81	8.26	1.55	Nb^{3+}/Nb	18.63		15.31	3.32
Sr^{2+}/Sr	9.06		7.53	1.53	Te^{4+}/Te	25.18		20.19	4.99
Ba^{2+}/Ba	8.37		6.85	1.52	Po^{2+}/Po	14.35		9.28	5.07
Ra^{2+}/Ra	8.21		6.71	1.50	Po^{3+}/Po	18.67		13.69	4.98
Zn^{2+}/Zn	14.18	14.17	10.51	3.66	Cr^{2+}/Cr	13.20		9.68	3.52
Cd^{2+}/Cd	13.37	13.36	9.34	4.02	Cr^{3+}/Cr	18.73		15.02	3.71
Hg^{2+}/Hg	14.75		9.48	5.27	Mn^{2+}/Mn		13.31	9.49	3.37
Al^{3+}/Al		18.70	15.95	2.75	Fe^{2+}/Fe	13.82		9.84	3.98
Ga^{2+}/Ga	14.47		10.50	3.97	Fe^{3+}/Fe	19.37	19.35	14.97	4.38
Ga^{3+}/Ga		19.89	15.99	3.90	Ru^{2+}/Ru	14.93		10.06	4.87
In^+/In	7.88		3.71	4.17	Os^{2+}/Os	15.36		10.24	5.12
In^{3+}/In		18.16	14.08	4.08	Co^{2+}/Co	14.63		10.49	4.14
Tl^+/Tl	7.64	7.64	3.56	4.08	Co^{3+}/Co	21.07		16.25	4.82
Tl^{3+}/Tl	19.30		14.17	5.13	Rh^{3+}/Rh	20.55		15.33	5.22
Sc^{3+}/Sc	15.90		13.56	2.34	Ni^{2+}/Ni	14.91		10.74	4.17
Y^{3+}/Y	14.36		12.31	2.05	Pd^{2+}/Pd	15.67		10.26	5.41
La^{3+}/La	13.19		11.14	2.05	Pt^{2+}/Pt	16.08		10.46	5.62
Ce^{3+}/Ce		14.16	12.22	1.94	$F^-/\frac{1}{2}F_2$		2.77	−4.30	7.07
Ce^{4+}/Ce	19.84		16.88	2.96	$Cl^-/\frac{1}{2}Cl_2$	2.65	2.71	−3.07	5.78
Nd^{3+}/Nd	13.98		12.00	1.98	$Br^-/\frac{1}{2}Br_2$	2.66	2.68	−2.81	5.49
Sm^{3+}/Sm	14.26		12.25	2.01	$I^-/\frac{1}{2}I_2$	2.51	2.48	−2.48	4.95
Gd^{3+}/Gd	14.40		12.38	2.02	e^-_{aq}			−1.56[6]	1.56

where the superscript o signifies the standard state and the subscript g the gaseous state. ΔF_i^o is then given by the standard heat of formation $\Delta \bar{H}_i^o$ and the standard change of entropy ΔS_i^o associated with the formation of $M_{i,g}^{z_i}$ and gaseous electrons from the element M_i, as

$$\Delta F_i^o = \Delta \bar{H}_i^o - T\Delta S_i^o , \tag{4}$$

where

$$\Delta \bar{H}_i^o = \bar{H}_{i,g}^o + z_i \bar{H}_{e,g}^o - \bar{H}_{M_i}^o , \tag{5}$$

$$\Delta S^o = S_{i,g}^o + z_i S_{e,g}^o - S_{M_i}^o . \tag{6}$$

The values of $\Delta \bar{H}_i^o$ and of $S_{M_i}^o$ are quoted from the table of the NBS.[3] The values of $S_{i,g}^o$ are calculated by the equation for monoatomic gas,[4] neglecting the entropy term of the electronic states,

$$S_{i,g}^o = \frac{3}{2} R \ln m_i + \frac{5}{2} R \ln T - 2.31 , \tag{7}$$

where m_i is the molecular weight of the element M_i. The value of $S_{e,g}^o$ is similarly estimated by Eq. (7) as 3.62 *e. u.* at 25°C.

The values of $-\frac{1}{z_i}\alpha_{i,aq}^o$ and of $\phi_{i,aq}^o$ at 25°C thus calculated are summarized in the Table. For comparison the values of $\Delta F_i^o/z_i$ (El. Ch.) are shown in the table which are obtained electrochemically by Eq. (2) using the values of $\phi_{i,aq}^o$ and those of $\alpha_{i,aq}^o$ estimated by Randles.[5]

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