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Author(s)	NOTOYA, Reiko; MATSUDA, Akiya
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STANDARD MOLAL REAL FREE ENERGIES
OF SOLVATION OF MONOATOMIC
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POTENTIALS IN FUSED SALTS

By

Reiko Notoya[*] and Akiya Matsuda[*]

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Abstract

The standard molal real free energies of solvation of monoatomic ions $-\alpha^{0}$'s and the absolute electrode potentials φ_i^0's of the associated redox systems in fused salts have been estimated by an empirical method proposed previously for 40 ionic species from quadruvalent cations to monovalent anions.

It has been found that α^{0}'s in fused salts are proportional to those in water with proportionality constants close to unity.

1. Introduction

The standard free energy of formation ΔF_1^0 of a gaseous monoatomic ion $M_i^{z_i}$ from its element M_i may be expressed at given temperature as the sum of the standard molal real free energy of solvation of the ion $-\alpha_i^0$ in a given solvent and the absolute electrode potential φ_i^0 of the redox system $M_i^{z_i}/M_i$ as deduced in a previous work[1]

$$\Delta F_1^0 = -\alpha_i^0 + z_i F \varphi_i^0, \qquad (1)$$

where F is the Faraday and φ_i^0 is referred to the standard state of the electron in gaseous state at the given temperature. When the value of $-\alpha_i^0$ is given, the value of φ_i^0 may be estimated on the basis of Eq. (1) using the thermodynamical data for ΔF_1^0.

In the present work the values of $-\alpha_i^0$ and φ_i^0 will be estimated for a series of monoatomic ions in fused salts by the empirical method developed in a previous work[1] on the basis of the standard electrode potentials of the associated redox systems.

2. The basic concept of the empirical method

The usual standard electrode potential $E^o_{ij}(T)$ of the redox system $M^{z_i}_i/$ M_i in a fused salt referred to an appropriate reference electrode $M^{z_j}_j/M_j$ at a given temperature T and that in aqueous solution $E^o_{ij,aq}(298)$ at 25°C are given by the difference of the absolute potentials of the respective electrodes

$$E^o_{ij}(T) = \varphi^o_i(T) - \varphi^o_j(T), \qquad (2\,a)$$

$$E^o_{ij,aq}(298) = \varphi^o_{i,aq}(298) - \varphi^{o}_{j,aq}(298) \qquad (2\,b)$$

Using Eqs. (1)–(2 b), we have an expression for the relative value of the free energy of solvation of the ion $M^{z_i}_i$ to that of the reference ion $M^{z_j}_j$ in a fused salt as[2]

$$-\frac{1}{z_i}\alpha^o_i(T) + \frac{1}{z_j}\alpha^o_j(T) = a_{ij} + b_{ij} \qquad (3)$$

where

$$a_{ij} = -\frac{1}{z_i}\alpha^o_{i,aq}(298) + \frac{1}{z_j}\alpha^o_{j,aq}(298) - F\Delta E^o_{ij} \qquad (4)$$

$$b_{ij} = \frac{1}{z_i}\left\{\Delta F^o_i(T) - \Delta F^o_i(298)\right\} - \frac{1}{z_j}\left\{\Delta F^o_j(T) - \Delta F^o_j(298)\right\} \qquad (5)$$

$$\Delta E^o_{ij} = E^o_{ij}(T) - E^o_{ij,aq}(298). \qquad (6)$$

It can be seen from Eqs. (3)–(6) that the relative value of $-\frac{1}{z_i}\alpha^o_i(T) +$ $\frac{1}{z_j}\alpha^o_j(T)$ in a fused salt is a quantity which can be evaluated, since a_{ij} is given by the relative free energies of hydration at 25°C and the standard electrode potential referred to that in water which are all known quantities and b_{ij} is given by the free energies of formation of gaseous ions at T and 25°C which can be estimated from the thermodynamical data.

If we assume here an ideal ion which should exhibit no interaction with any solvent, i. e., $\alpha^o_i(T) = \alpha^o_{i,aq}(298) = 0$, then the value of $a_{ij} + b_{ij}$ for such an ideal ion gives the free energy of solvation of the reference ion $\frac{1}{z_j}\alpha^o_j(T)$, as readily seen from Eq. (3). When the value of $\frac{1}{z_j}\alpha^o_j(T)$ is given, it may be possible to estimate the value of $-\alpha^o_i(T)$ from Eq. (3) and the value of $\varphi^o_i(T)$ from Eq. (1).

However, such an ideal ion should exist, if any, as a limiting approach of the ions in real systems, for instance, as the limiting value of $a_{ij} + b_{ij}$

Free Energies of Solvation of Ions and Absolute Potentials in Fused salts

TABLE I. Standard free energies of formation of gaseous monoatomic ions from elements $\frac{1}{z_i} \Delta F_1^o (T)$ in electron volts

Temperature / Electrode	450°C 723.15°K	475°C 748.15°K	150°C 423.15°K	177°C 450.15°K	250°C 523.15°K	625°C 898.15°K	161.85°C 435°K	221.85°C 495°K	700°C 973.15°K	550°C 823.15°K	25°C 298.15°K
$H^+/\frac{1}{2}H_2$	15.38	15.35	15.63	15.61	15.55	15.21	15.62	15.57	15.14	15.28	15.72
Li^+/Li	6.13	6.10	6.52	6.49	6.39	5.89	6.51	6.43	5.79	5.99	6.67
Na^+/Na	5.46	5.43	5.82	5.79	5.70	5.23	5.81	5.73	5.14	5.33	5.97
Cu^+/Cu	10.16	10.12	10.68**	10.61	10.49	9.86	10.63	10.54	9.74	9.99	10.85
Cu^{2+}/Cu	15.10	15.08	15.44**	15.40	15.32	14.90	15.41	15.35	14.82	14.99	15.58
Ag^+/Ag	9.51	9.46	10.01**	9.95	9.83	9.21	9.97	9.87	9.09	9.34	10.19
Be^{2+}/Be	14.83	14.80	15.14	15.11	15.04	14.64	15.12	15.07	14.56	14.72	15.25
Mg^{2+}/Mg	11.57	11.55	11.85	11.83	11.76	11.40	11.84	11.79	11.33	11.47	11.96
Zn^{2+}/Zn	13.78	13.75	14.06	14.04	13.97	13.61	14.05	14.00	13.54	13.68	14.18
Cd^{2+}/Cd	12.98	12.96	13.25	13.23	13.16	12.81	13.24	13.19	12.74	12.89	13.37
Al^{3+}/Al	18.39	18.37	18.62	18.60	18.54	18.24	18.61	18.56	18.18	18.30	18.70
Ga^{3+}/Ga	19.61	19.59	19.82**	19.80	19.75	19.47	19.81	19.77	19.42	19.53	19.89
In^{3+}/In	17.87	17.86	18.08	18.06	18.01	17.74	18.07	18.03	17.68	17.80	18.16
Tl^+/Tl	7.04	7.01	7.47	7.43	7.32	6.80	7.45	7.36	6.69	6.90	7.64
Sc^{3+}/Sc	15.59	15.57	15.82	15.80	15.75	15.45	15.81	15.77	15.39	15.51	15.90
Y^{3+}/Y	14.05	14.03	14.28	14.26	14.21	13.91	14.27	14.23	13.85	13.97	14.36
La^{3+}/La	12.89	12.87	13.11	13.09	13.04	12.75	13.10	13.06	12.69	12.81	13.19
Ce^{3+}/Ce	13.84	13.82	14.07	14.05	14.06	13.69	14.06	14.02	13.63	13.76	14.16
Nd^{3+}/Nd	13.66	13.64	13.89	13.87	13.82	13.51	13.88	13.84	13.45	13.57	13.98
Gd^{3+}/Gd	14.09	14.07	14.32	14.30	14.24	13.95	14.31	14.26	13.89	14.01	14.40
Th^{4+}/Th	18.95	18.93	19.15	19.13	19.09	18.83	19.14	19.10	18.77	18.88	19.22
U^{3+}/U	14.23	14.20	14.48	14.45	14.39	14.07	14.47	14.42	14.00	14.14	14.57
Sn^{2+}/Sn	12.01	11.99	12.27	12.25	12.18	11.84	12.26	12.21	11.78	11.92	12.38
Pb^{2+}/Pb	11.68	11.66	11.95	11.92	11.86	11.52	11.94	11.89	11.45	11.59	12.07
Ti^{2+}/Ti	12.01	11.98	12.33	12.30	12.22	11.81	12.31	12.25	11.73	11.90	12.45
Zr^{4+}/Zr	20.76	20.74	20.96	20.94	20.89	20.63	20.95	20.91	20.57	20.68	21.03
Hf^{4+}/Hf	19.71	19.69	19.91	19.89	19.84	19.58	19.90	19.86	19.52	19.63	19.98
V^{2+}/V	12.39	12.36	12.71	12.68	12.60	12.19	12.69	12.63	12.10	12.28	12.83
Cr^{2+}/Cr	12.77	12.75	13.01***	13.05	12.98	12.58	13.07	13.01	12.50	12.66	13.20
Cr^{3+}/Cr	18.38	18.35	18.63	18.61	18.55	18.22	18.63	18.58	18.15	18.29	18.73
$Cl^-/\frac{1}{2}Cl_2$	2.763	2.76	2.73	2.74	2.75	2.768	2.735	2.743	2.768	2.767	2.65
$Br^-/\frac{1}{2}Br_2$	2.742	2.74	2.72	2.72	2.73	2.745	2.72	2.726	2.744	2.744	2.66
$I^-/\frac{1}{2}I_2$	2.618	2.62	2.58	2.59	2.61	2.617	2.586	2.606	2.614	2.618	2.51
Mn^{2+}/Mn	12.87	12.84	13.19	13.16	13.08	12.67	13.18	13.11	12.59	12.76	13.31
Fe^{2+}/Fe	13.36	13.33	13.69	13.66	13.58	13.16	13.68	13.61	13.07	13.24	13.82
Fe^{3+}/Fe	19.00	18.98	19.25	19.23	19.17	18.84	19.25	19.20	18.77	18.91	19.37
Co^{2+}/Co	14.17	13.88	14.23	14.48	14.40	13.97	14.49	14.43	13.88	14.06	14.63
Rh^{3+}/Rh	20.22	20.20	20.46	20.44	20.38	20.06	20.45	20.41	20.00	20.13	20.55
Ni^{2+}/Ni	14.46	14.43	14.78	14.76	14.68	14.25	14.77	14.71	14.17	14.34	14.91
Pd^{2+}/Pd	15.21	15.18	15.54	15.52	15.44	15.01	15.53	15.47	14.92	15.10	15.67
Pt^{2+}/Pt	15.62	15.59	15.59	15.92	15.84	15.41	15.94	15.87	15.32	15.50	16.08

extrapolated to $-\dfrac{1}{z_i}\alpha^o_{i,aq}(298)=0$ when $a_{ij}+b_{ij}$ is plotted against $-\dfrac{1}{z_i}\alpha^o_{i,aq}$ (298) for a series of real ions.

3. Graphic presentation of $a_{ij}+b_{ij}$ vs. $-\dfrac{1}{z_i}\alpha^o_{i,aq}(298)$

The values of a_{ij} for a series of monoatomic ions in fused salts were estimated in a previous work[2]. The values of b_{ij} for these ions are estimated in the present work using the values of ΔF^o_i's at a temperature T and 298°K. The thermodynamical data used for the calculation of ΔF^o_i are those in the tables of JANAF[3], Samsonov[4], Ryabin *et al*[5], CRC Handbook of Weast and Astle[6] and Matsuda[7]. The standard electrode potentials in
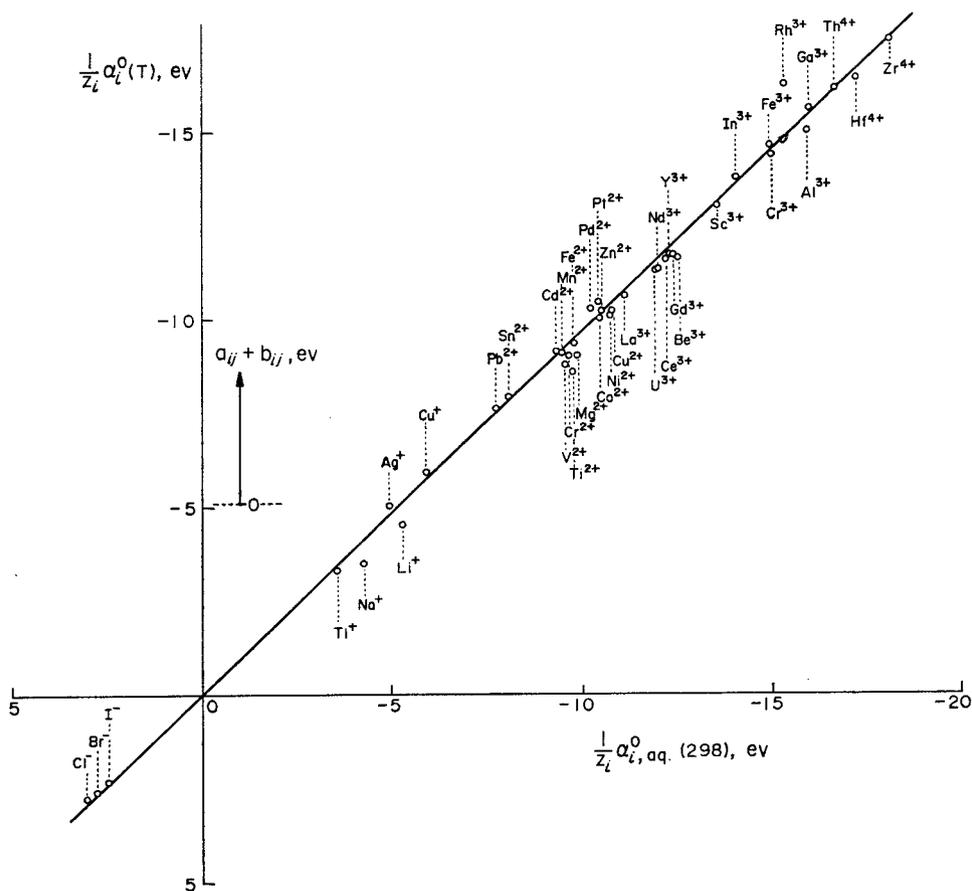

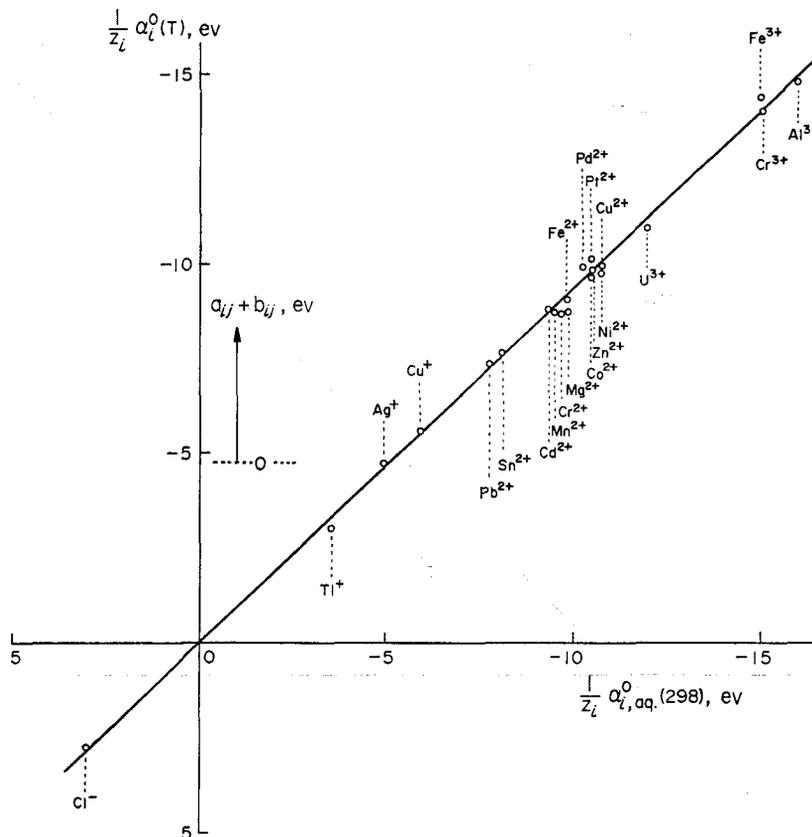**Fig. 1.** $\dfrac{1}{z_i}\alpha^o_i(T)$ vs. $\dfrac{1}{z_i}\alpha^o_{i,aq}(298)$ in LiCl–KCl at 450°C.

Fig. 2. $\frac{1}{z_i} \alpha_i^o(T)$ vs. $\frac{1}{z_i} \alpha_{i,aq}^o(298)$ in $MgCl_2$-$NaCl$-KCl at 475C°.

molal scale in fused salts are quoted from the table of Plambeck[8] and those in water from Dobos[9]. The values of $\Delta F_i^o/z_i$ estimated for monoatomic ions are listed in Table I, where the double asterisks ** in the column of 423°K means the value of ΔF_i^o at 408°K and *** that at 491°K which are quite close to that at 423°K within the accuracy of the present treatment.

The values of $a_{ij} + b_{ij}$ estimated in this way for a number of mono-atomic ions in fused salts are plotted against the values of $-\frac{1}{z_i} \alpha_{i,aq}^o(298)$ in Figs. (1)–(10). In these Figures the values of $a_{ij} + b_{ij}$ for an ion is measured from that of the reference ion which is chosen arbitrarily on the vertical axis.
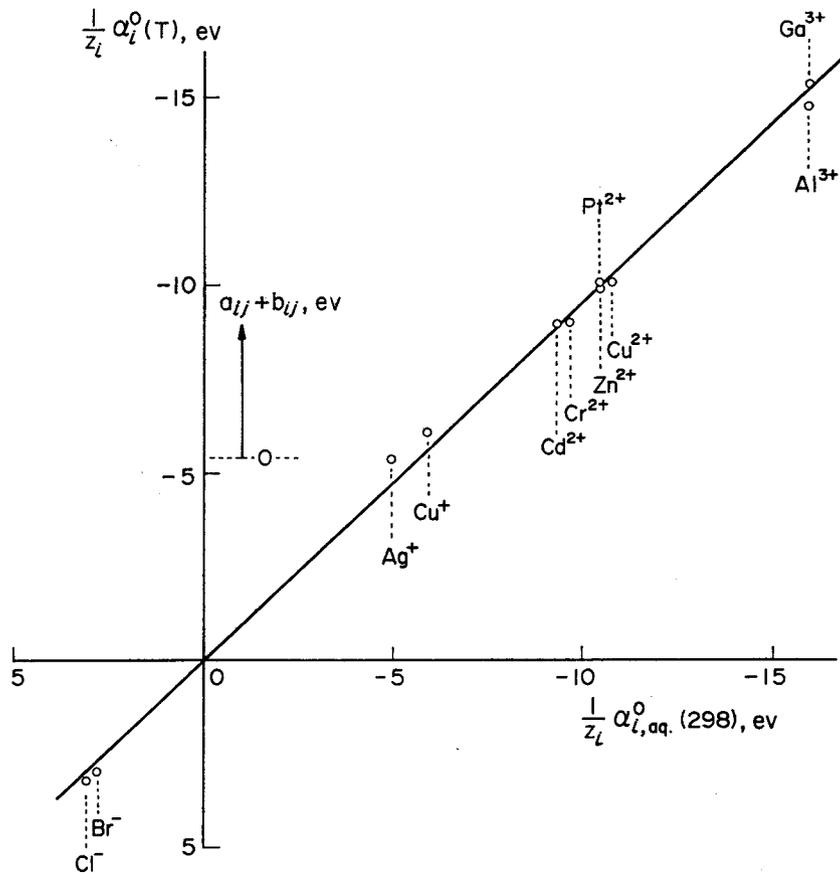
Fig. 3. $\frac{1}{z_i}\,\alpha_i^{\circ}(T)$ vs. $\frac{1}{z_i}\,\alpha_{i,aq}^{\circ}(298)$ in $AlCl_3$-$NaCl$-KCl at 150°C.

4. Estimation of $-\dfrac{1}{z_j}\,\alpha_j^{\circ}(T)$ and $\varphi_j^{\circ}(T)$

It can be seen from these Figures that $a_{ij}+b_{ij}$ changes linearly with $-\dfrac{1}{z_i}\,\alpha_{i,aq}^{\circ}(298)$ as

$$a_{ij}+b_{ij} = a_0 + \beta x \qquad (7)$$

where x denotes $-\dfrac{1}{z_i}\,\alpha_{i,aq}^{\circ}(298)$, β is a constant characteristic to the solvent. a_0 is the value of $a_{ij}+b_{ij}$ which is obtained from the intersection of this line with the vertical axis, and a_0 may reveal $\dfrac{1}{z_j}\,\alpha_j^{\circ}(T)$ for the reference

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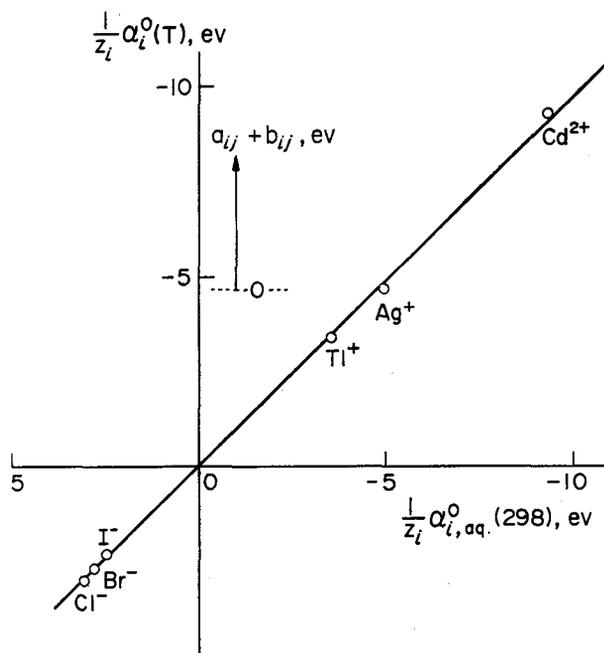

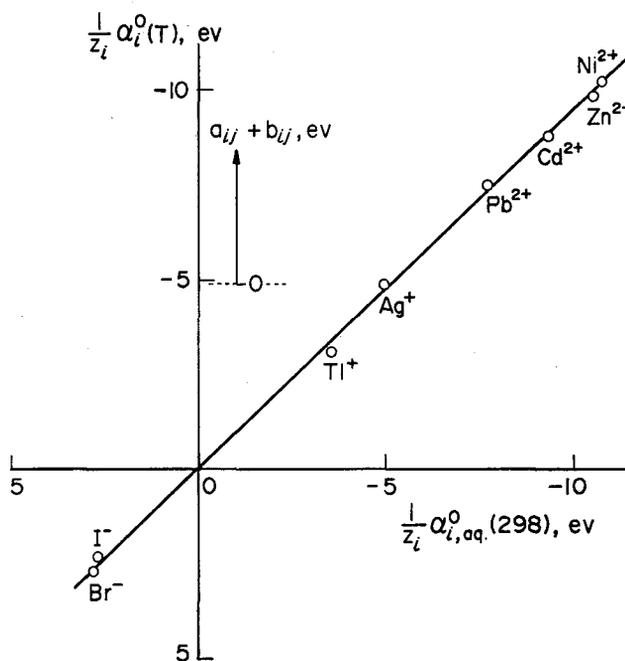**Fig. 4.** $\frac{1}{z_1} \alpha_1^0(T)$ vs. $\frac{1}{z_1} \alpha_{1,aq}^0(298)$ in $LiNO_3$–KNO_3 at $177°C$.

Fig. 5. $\frac{1}{z_1} \alpha_1^0(T)$ vs. $\frac{1}{z_1} \alpha_{1,aq}^0(298)$ in $NaNO_3$–KNO_3 at $250°C$.
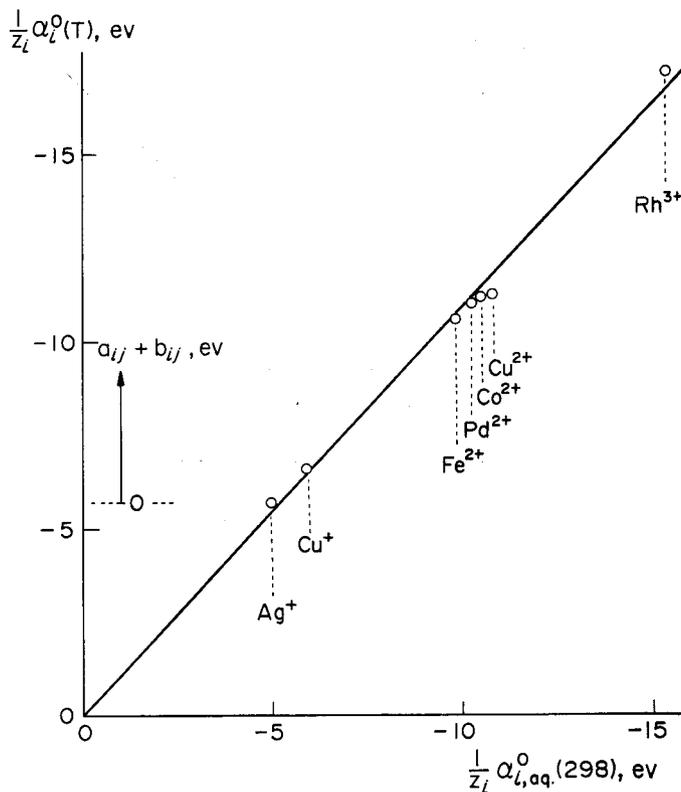
Fig. 6. $\frac{1}{z_i}\alpha_i^o(T)$ vs. $\frac{1}{z_i}\alpha_{i,aq}^o(298)$ in Li_2SO_4-K_2SO_4 at 625°C.

ion according to Eqs. (3) and (7), since $-\dfrac{1}{z_i}\alpha_i^o(T)$ may be assumed to be zero at x=0.

In this way we have a proportionality relation between $-\dfrac{1}{z_i}\alpha_i^o(T)$ and x from the linearlity between $\boldsymbol{a}_{ij}+\boldsymbol{b}_{ij}$ and x on the basis of Eqs. (7) and (3),

$$-\frac{1}{z_i}\alpha_i^o(T) = \beta x, \tag{8}$$

which is also shown by the same line of $\boldsymbol{a}_{ij}+\boldsymbol{b}_{ij}$ vs. x with the origin on the vertical axis displaced by $\boldsymbol{a}_0$, as shown in these Figures.

The values of $-\alpha_j^o(T)$ for the reference ion, the absolute potential $\varphi_j^o(T)$ for the reference electrode and the proportionality constant β are listed in Table I for a series of fused salts. It is surprising that β is quite

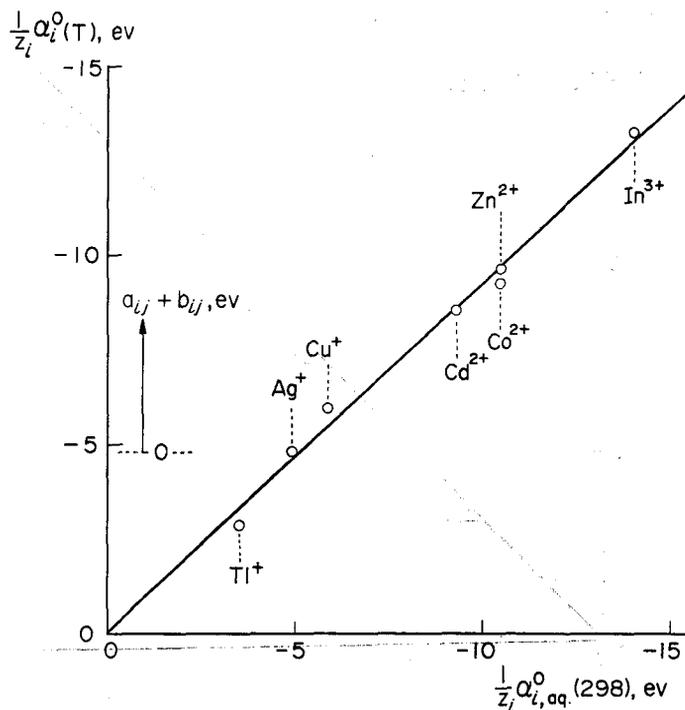*Free Energies of Solvation of Ions and Absolute Potentials in Fused salts*

Fig. 7. $\dfrac{1}{z_i}\,\alpha_i^0(T)$ vs. $\dfrac{1}{z_i}\,\alpha_{i,aq}^0(298)$ in NaSCN-KSCN at 161.85°C.

TABLE II. Standard molal real free energies of solvation of reference ions, absolute potentials of reference electrodes, and proportionality constant β in fused salts, standard deviation $\pm\sigma$ of $-\dfrac{1}{z_i}\,\alpha_i^0(T)$ from Eq. (8).

Fused Salt	Temp. (K)	Reference Ion	$-\dfrac{1}{z_j}\,\alpha_j^0(T)$ (ev)	$\varphi_j^0(T)$ (v)	β	$\pm\sigma$ (ev)
LiCl-KCl	723	Ag^+	5.08	4.43	0.955	0.23
MgCl₂NaCl-KCl	748	Ag^+	4.77	4.69	0.932	0.23
AlCl₃-NaCl-KCl	423	Ag^+	5.39	4.62	0.951	0.30
LiNO₃-KNO₃	450	Ag^+	4.65	5.30	0.974	0.11
NaNO₃-KNO₃	523	Ag^+	4.88	4.95	0.946	0.13
Li₂SO₄-K₂SO₄	898	Ag^+	5.71	3.50	1.087	0.30
NaSCN-KSCN	435	Ag^+	4.83	5.14	0.922	0.33
CH₃COOLi-CH₃COONa-CH₃COOK	495	Zn^{++}	10.77	3.23	1.026	0.05
NaPO₃-KPO₃	973	Ag^+	4.88	4.12	0.990	0.03
Li₂CO₃-Na₂CO₃	823	Ag^+	5.06	4.29	1.019	0.02

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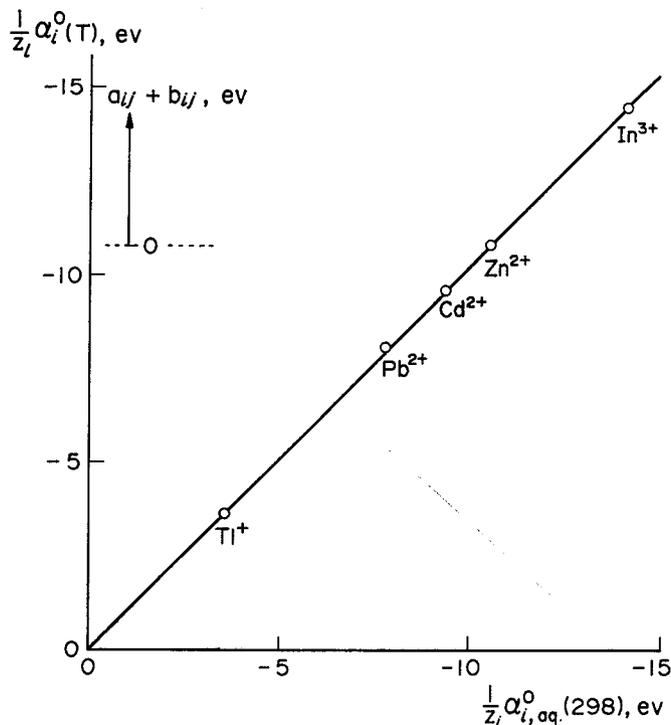
Fig. 8. $\frac{1}{z_i}\alpha_i^0(T)$ vs. $\frac{1}{z_i}\alpha_{i,aq}^0(298)$ in CH_3COOLi–CH_3COONa–CH_3COOK at $221.85°C$.

close to unity in any fused salt available as in the case of organic and inorganic non-aqueous solvents reported in the previous work[1]. The standard deviation $\pm\sigma$ of $-\frac{1}{z_i}\alpha_i^0(T)$ from the proportionality relation Eq. (8) are found in fused salts to be less than 0.33 ev from Table II.

5. Estimation of $-\frac{1}{z_i}\alpha_i^0(T)$ and $\varphi_i^0(T)$

The values of $-\frac{1}{z_i}\alpha_i^0(T)$ of the ions given in Figs. (1)–(10) are listed in Table III. The values of $-\frac{1}{z_i}\alpha_i^0(T)$ of the ions for which we have no experimental data of the standard electrode potential of the associated redox system can be calculated from Eq. (8) using the value of β obtained from the Figures. The values of $-\frac{1}{z_i}\alpha_i^0(T)$ calculated in this way are

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Fig. 9. $\frac{1}{z_i}\,\alpha_i^0(T)$ vs. $\frac{1}{z_i}\,\alpha_{i,aq}^0(298)$ in $NaPO_3-KPO_3$ at $700°C$.

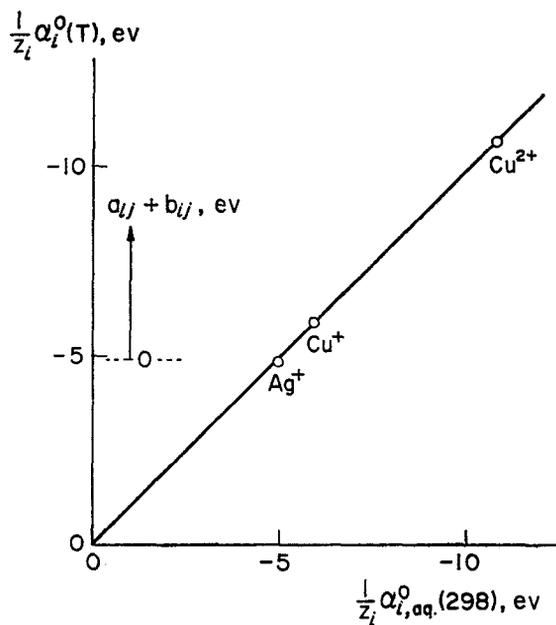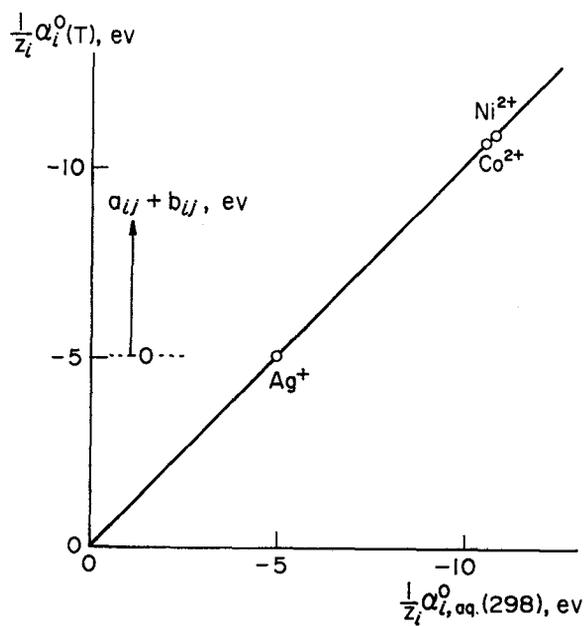**Fig. 10.** $\frac{1}{z_i}\,\alpha_i^0(T)$ vs. $\frac{1}{z_i}\,\alpha_{i,aq}^0(298)$ in $Li_2CO_3-Na_2CO_3$ at $550°C$.

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TABLE III Standard molal real free energies of solvation
of monoatomic ions in fused salts $-\frac{1}{z_i}\,\alpha_i^o(T)$
in electron volts[#]

Temperature $M_i{}^{z_i}$	450°C 723.15 °K	475°C 748.15 °K	150°C 423.15 °K	177°C 450.15 °K	250°C 523.15 °K	625°C 898.15 °K	161.85 °C 435°K	221.85 °C 495°K	700°C 973.15 °K	550°C 823.15 °K	25°C 298.15 °K
H^+	10.79*	10.54*	10.75*	11.01*	10.69*	12.29*	10.41*	11.60*	11.19*	11.52*	11.30
Li^+	4.56	4.94*	5.04*	5.16*	5.01*	5.76*	4.88*	5.44*	5.25*	5.40*	5.30
Na^+	3.53	3.97*	4.05*	4.15*	4.03*	4.63*	3.93*	4.37*	4.22*	4.34*	4.26
Cu^+	5.95	5.61	6.07	5.76*	5.59*	6.57	5.94	6.07*	5.88	6.03*	5.91
Cu^{2+}	10.21	9.96	10.07	10.50*	10.20*	11.29	9.93*	11.06*	10.67	10.99*	10.78
Ag^+	5.08	4.77	5.39	4.65	4.88	5.71	4.83	5.09*	4.88	5.06	4.96
Be^{2+}	11.72	11.68*	11.92*	12.21*	11.86*	13.62*	11.55*	12.86*	12.40*	12.77*	12.53
Mg^{2+}	9.00	8.74	9.40*	9.88*	9.35*	10.74*	9.10*	10.14*	9.78*	10.07*	9.88
Zn^{2+}	10.19	9.85	9.92	10.24*	9.84	11.43*	9.63	10.77	10.40*	10.71*	10.51
Cd^{2+}	9.14	8.81	8.95	9.25	8.78	10.16*	8.55	9.58	9.24*	9.52*	9.34
Al^{3+}	15.00	14.80	14.74	15.54*	15.09*	17.34*	14.70*	16.37*	15.79*	16.26*	15.95
Ga^{3+}	15.59	14.91*	15.34	15.58*	15.13*	17.39*	14.74*	16.41*	15.83*	16.30*	15.99
In^{3+}	13.76	13.13*	13.39*	13.72*	13.32*	15.31*	13.20	14.43	13.94*	14.35*	14.08
Tl^+	3.34	3.08	3.39*	3.39	3.11	3.87*	2.85	3.61	3.52*	3.63*	3.56
Sc^{3+}	13.00	12.64*	12.90*	13.21*	12.83*	14.74*	12.50*	13.92*	13.42*	13.82*	13.56
Y^{3+}	11.74	11.48*	11.71*	11.99*	11.65*	13.38*	11.34*	12.63*	12.18*	12.55*	12.31
La^{3+}	10.59	10.39*	10.60*	10.85*	10.54*	12.11*	10.27*	11.43*	11.03*	11.36*	11.14
Ce^{3+}	11.60	11.39*	11.62*	11.90*	11.56*	13.29*	11.26*	12.54*	12.10*	12.46*	12.22
Nd^{3+}	11.33	11.19*	11.42*	11.69*	11.35*	13.05*	11.06*	12.32*	11.88*	12.23*	12.00
Gd^{3+}	11.73	11.54*	11.78*	12.06*	11.71*	13.46*	11.41*	12.71*	12.25*	12.62*	12.38
Th^{4+}	16.12	15.57*	15.89*	16.27*	15.80*	18.16*	15.39*	17.14*	16.53*	17.02*	16.70
U^{3+}	11.29	10.95	11.37*	11.64*	11.31*	12.99*	11.01*	12.26*	11.83*	12.18*	11.95
Sn^{2+}	7.94	7.68	7.71*	7.89*	7.66*	8.81*	7.46*	8.31*	8.02*	8.26*	8.10
Pb^{2+}	7.63	7.38	7.38*	7.56*	7.48	8.44*	7.15*	8.06	7.68*	7.91*	7.76
Ti^{2+}	8.59	9.12*	9.30*	9.53*	9.25*	10.63*	9.01*	10.04*	9.68*	9.97*	9.78
Zr^{4+}	17.42	16.91*	17.26*	17.67*	17.16*	19.72*	16.72*	18.62*	17.96*	18.49*	18.14
Hf^{4+}	16.17	16.09*	16.42*	16.81*	16.33*	18.77*	15.91*	17.71*	17.08*	17.60*	17.26
V^{2+}	8.77	8.94*	9.12*	9.34*	9.07*	10.43*	8.84*	9.84*	9.49*	9.78*	9.59
Cr^{2+}	9.04	8.69	9.02	9.43*	9.16*	10.52*	8.92*	9.93*	9.58*	9.87*	9.68
Cr^{3+}	14.36	14.04	14.29*	14.63*	14.21*	16.33*	13.84*	15.42*	14.87*	15.31*	15.02
Cl^-	−2.698	−2.750	−3.198	−3.01	−2.90*	−3.34*	−2.83*	−3.15*	−3.04*	−3.13*	−3.07
Br^-	−2.547	−2.62*	−2.946	−2.70	−2.68	−3.06*	−2.59*	−2.88*	−2.78*	−2.86*	−2.81
I^-	−2.288	−2.31*	−2.36*	−2.34	−2.29	−2.70*	−2.29*	−2.55*	−2.45*	−2.53*	−2.48
Mn^{2+}	9.11	8.73	9.03*	9.24*	8.98*	10.32*	8.75*	9.74*	9.39*	9.67*	9.49
Fe^{2+}	9.38	9.06	9.36*	9.59*	9.31*	10.58	9.07*	10.10*	9.74*	10.03*	9.84
Fe^{3+}	14.61	14.38	14.24*	14.58*	14.16*	16.28*	13.80*	15.36*	14.82*	15.26*	14.97
Co^{2+}	10.01	9.98*	10.22*	10.46*	9.93*	11.18	9.23	10.77*	10.38*	10.72	10.49
Rh^{3+}	16.26	14.29*	14.58*	14.93*	14.50*	17.17	14.13*	15.73*	15.17*	15.63*	15.33
Ni^{2+}	10.10	9.77	10.22*	10.46*	10.22	11.68*	9.90*	11.02*	10.63*	10.92	10.74
Pb^{2+}	10.27	9.93	9.76*	9.99*	9.71*	10.97	9.45*	10.53*	10.16*	10.46*	10.26
Pt^{2+}	10.46	10.13	10.08	10.19*	9.90*	11.37*	9.64*	10.74*	10.35*	10.66*	10.46
e^-	−1.49*	−1.45*	−1.48*	−1.52*	−1.48*	−1.70*	−1.44*	−1.60*	−1.54*	−1.59*	−1.56

Free Energies of Solvation of Ions and Absolute Potentials in Fused salts

TABLE IV   Absolute electrode potentials $\varphi_i^o(T)$
in fused salts[#]

Temperature / Electrode	450°C 723.15 °K	475°C 748.15 °K	150°C 423.15 °K	177°C 450.15 °K	250°C 523.15 °K	625°C 898.15 °K	161.85 °C 435°K	221.85 °C 495°K	700°C 973.15 °K	550°C 823.15 °K	25°C 298.15 °K
$H^+/\frac{1}{2}H_2$	4.59*	4.81*	4.88*	4.60*	4.86*	2.92*	5.21*	3.97*	3.96*	3.76*	4.42
Li^+/Li	1.57	1.16*	1.48*	1.33*	1.38*	0.13*	1.63*	0.99*	0.54*	0.59*	1.40
Na^+/Na	1.93	1.46*	1.77*	1.64*	1.67*	0.60*	1.88*	1.36*	0.92*	0.99*	1.71
Cu^+/Cu	4.21	4.51	4.61	4.85*	4.90*	3.29	4.69	4.47*	3.85	3.96*	4.94
Cu^{2+}/Cu	4.89	5.12	5.37	4.90*	5.12*	3.61	5.48$_*$	4.29*	4.15	4.00*	4.77
Ag^+/Ag	4.43	4.69	4.62	5.30	4.95	3.50	5.14	4.78*	4.12	4.29	5.22
Be^{2+}/Be	3.12	3.12*	3.22*	2.90*	3.18*	1.02*	3.57*	2.21*	2.16*	1.95*	2.72
Mg^{2+}/Mg	2.57	2.81	2.45*	1.95*	2.41*	0.66*	2.74*	1.65*	1.55*	1.40*	2.08
Zn^{2+}/Zn	3.59	3.90	4.14	3.80*	4.13	2.18*	4.42	3.23	3.14*	2.97*	3.66
Cd^{2+}/Cd	3.84	4.15	4.31	3.98	4.38	2.65*	4.69	3.61	3.50*	3.37*	4.02
Al^{3+}/Al	3.39	3.57	3.88	3.06*	3.45*	0.90*	3.91*	2.19*	2.39*	2.04*	2.75
Ga^{3+}/Ga	4.01	4.68*	4.48	4.22*	4.62*	2.08*	5.07*	3.36*	3.59*	3.23*	3.90
In^{3+}/In	4.12	4.73*	4.69*	4.34*	4.69*	2.43*	4.87	3.60	3.74*	3.45*	4.08
Tl^+/Tl	3.70	3.93	4.08*	4.04	4.12	2.93*	4.60	3.75	3.17*	3.27*	4.08
Sc^{3+}/Sc	2.60	2.93*	2.92*	2.59*	2.92*	0.71*	3.31*	1.85*	1.97*	1.69*	2.34
Y^{3+}/Y	2.32	2.55*	2.57*	2.27*	2.56*	0.53*	2.93*	1.60*	1.67*	1.42*	2.05
La^{3+}/La	2.30	2.48*	2.51*	2.24*	2.50*	0.64*	2.83*	1.63*	1.66*	1.45*	2.05
Ce^{3+}/Ce	2.24	2.43*	2.45*	2.15*	2.50*	0.40*	2.80*	1.48*	1.53*	1.30*	1.94
Nd^{3+}/Nd	2.33	2.45*	2.47*	2.18*	2.47*	0.46*	2.82*	1.52*	1.57*	1.34*	1.98
Gd^{3+}/Gd	2.36	2.53*	2.54*	2.24*	2.53*	0.49*	2.90*	1.55*	1.64*	1.39*	2.02
Th^{4+}/Th	2.84	3.36*	3.26*	2.86*	3.29*	0.67*	3.75*	1.96*	2.24*	1.86*	2.52
U^{3+}/U	2.93	3.25	3.11*	2.81*	3.08*	1.08*	3.46*	2.16*	2.17*	1.96*	2.62
Sn^{2+}/Sn	4.07	4.31	4.56*	4.36*	4.52*	3.03*	4.80*	3.90*	3.76*	3.66*	4.28
Pb^{2+}/Pb	4.05	4.28	4.57*	4.36*	4.38	3.08*	4.79*	3.83	3.77*	3.68*	4.29
Ti^{2+}/Ti	3.42	2.36*	3.03*	2.77*	2.97*	1.18*	3.30*	2.21*	2.05*	1.93*	2.67
Zr^{4+}/Zr	3.34	3.83*	3.70*	3.27*	3.73*	0.91*	4.23*	2.29*	2.61*	2.19*	2.89
Hf^{4+}/Hf	3.54	3.60*	3.49*	3.08*	3.51*	0.81*	3.99*	2.15*	2.44*	2.03*	2.72
V^{2+}/V	3.62	3.42*	4.59*	3.34*	3.53*	1.76*	3.85*	2.79*	2.61*	2.50*	3.24
Cr^{2+}/Cr	3.73	4.06	3.99	3.62*	3.82*	2.06*	4.15*	3.08*	2.92*	2.79*	3.52
Cr^{3+}/Cr	4.02	4.31	4.34*	3.98*	4.34*	1.89*	4.79*	3.16*	3.28*	2.98*	3.71
$Cl^-/\frac{1}{2}Cl_2$	5.46	5.51	5.93	5.75	5.65*	6.11*	5.57*	5.89*	5.81*	5.90*	5.78
$Br^-/\frac{1}{2}Br_2$	5.29	5.36*	5.67	5.42	5.42	5.81*	5.31*	5.61*	5.52*	5.60*	5.49
$I^-/\frac{1}{2}I_2$	4.91	4.93*	4.94*	4.93	4.90	5.32*	4.88*	5.16*	5.06*	5.15*	4.95
Mn^{2+}/Mn	3.76	4.11	4.16*	3.92*	4.10*	2.35*	4.43*	3.37*	3.20*	3.09*	3.37
Fe^{2+}/Fe	3.98	4.27	4.33*	4.07*	4.27*	2.58	4.61*	3.51*	3.33*	3.21*	3.98
Fe^{3+}/Fe	4.39	4.60	5.01*	4.65*	5.01*	2.56*	5.45*	3.84*	3.95*	3.65*	4.38
Co^{2+}/Co	4.16	4.22	4.25*	4.26*	4.47*	2.79	5.26	3.66*	3.50*	3.34	4.14
Rh^{3+}/Rh	3.96	5.91*	5.88*	5.51*	5.88*	2.89	6.32*	4.68*	4.83*	4.50*	5.22
Ni^{2+}/Ni	4.36	4.66	4.56*	4.30*	4.46	2.57*	4.87*	3.69*	3.54*	3.42	4.17
Pd^{2+}/Pd	4.94	5.25	5.78*	5.53*	5.73*	4.04	6.08*	4.91*	4.76*	4.64*	5.41
Pt^{2+}/Pt	5.15	5.46	5.88	5.73*	5.94*	4.04*	6.30*	5.13*	4.97*	4.84*	5.62
e^-/e_m^-	1.49*	1.45*	1.48*	1.52*	1.48*	1.70*	1.44*	1.60*	1.54*	1.59*	1.56

[#]) The solvent for each column in Table III and IV is the fused salt in Table II specified with the same temperature, except water for the last column.

also listed in Table III with single asterisk *. The values of $-\dfrac{1}{z_i}\alpha^{o}_{i,aq}$ (298) in water are quoted from the previous work[7].

The values of $\varphi^{o}_i(T)$ calculated from the standard potential by Eq. (2 a) using the value of $\varphi^{o}_j(T)$ of the reference electrode are listed in Table IV. The values of $\varphi^{o}_i(T)$ calculated by Eq. (1) using the value of $-\dfrac{1}{z_i}\alpha^{o}_i(T)$ and ΔF^{o}_i are also listed in this Table with single asterisk *. The absolute potential in water at 25°C are quoted from the previous work.[7]

It is suggested that the proportionality of the free energies of solvation of monoatomic ions in non-aqueous media and in water may provide a key word for the theoretical approach to the elucidation of the solvation bonding. The numerical values of $-\alpha^{o}_i(T)$ and $\varphi^{o}_i(T)$ for monoatomic ions in fused salts estimated in the present work may play an essential role in the comparison of the absolute rate of the electron transfer reactions of these ions in different fused salts.

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