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Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 27(3), 119-128
Issue Date	1980-03
Doc URL	https://hdl.handle.net/2115/25065
Type	departmental bulletin paper
File Information	27(3)_P119-128.pdf

J. Res. Inst. Catalysis, Hokkaido Univ., Vol. 27 No. 3, pp. 119 to 128 (1979)

PROPORTIONALITY OF STANDARD MOLAL REAL FREE ENERGIES OF SOLVATION OF MONOATOMIC IONS IN FUSED SALTS AND IN WATER

By

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(Received November 27, 1979)

Abstract

An Empirical method proposed previously has been applied to the estimation of the standard molal real free energies of solvation α^{o}'s of monoatomic ions in fused salts on the basis of the standard electrode potentials. It has been found that the α^{o}-values in fused salts are proportional to those in water for a wide range of ionic species from quadruvalent cations to monovalent anions with the proportionality constant close to unity.

The standard molal real free energy of solvation α_{i}^{o} of a monoatomic ion $M_{i}^{z_i}$ in a fused salt may be connected with the standard electromotive force ϕ_{i}^{o} and the free energy of formation ΔF_{i}^{o} of the gaseous ion $M_{i,g}^{z_i}$ from its element M_i by the equation[1]

$$\Delta F_{i}^{o} = -\alpha_{i}^{o} + z_i F \phi_{i}^{o}, \qquad (1)$$

where F is the Faraday, the superscript o stands for the standard state, and ϕ_{i}^{o} is the standard electromotive force of a single electrode associated with the ion $M_{i}^{z_i}$ and its element M_i referred to the standard state of the gaseous electron, as discussed in a previous work.[1]

In fused salts the standard electrode potential of a redox system is usually measured against an appropriate reference electrode according as the chemical properties of the salts. Eq. (1) also holds in the reference electrode as well which is composed of an ion $M_{j}^{z_j}$ and its element M_j. Therefore the standard electrode potential E_{ij}^{o} in a fused salt at a given temperature T

$$E_{ij}^{o} = \phi_{i}^{o}(T) - \phi_{j}^{o}(T), \qquad (2)$$

is given by the equation,

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$$\mathrm{FE}^{\circ}_{ij} = \frac{1}{z_i}\left\{\Delta F^{\circ}_{i}(\mathrm{T}) + \alpha^{\circ}_{i}(\mathrm{T})\right\} - \frac{1}{z_j}\left\{\Delta F^{\circ}_{j}(\mathrm{T}) + \alpha^{\circ}_{j}(\mathrm{T})\right\} \tag{3}$$

as a function of the temperature.

The standard electrode potential in an aqueous solution $\mathrm{E}^{\circ}_{ij,aq}$ at 25°C is also given by the similar equation

$$\mathrm{FE}^{\circ}_{ij,aq}(298) = \frac{1}{z_i}\left\{\Delta F^{\circ}_{i}(298) + \alpha^{\circ}_{i,aq}(298)\right\} - \frac{1}{z_j}\left\{\Delta F^{\circ}_{j}(298) + \alpha^{\circ}_{j,aq}(298)\right\} \tag{4}$$

The difference between the standard electrode potentials in fused salt and aqueous solution

$$\Delta \mathrm{E}^{\circ}_{ij} = \mathrm{E}^{\circ}_{ij}(\mathrm{T}) - \mathrm{E}^{\circ}_{ij,aq}(298), \tag{5}$$

is given by the equation

$$\mathrm{F}\Delta \mathrm{E}^{\circ}_{ij} = \frac{1}{z_i}\left\{\Delta F^{\circ}_{i}(\mathrm{T}) - \Delta F^{\circ}_{i}(298)\right\} - \frac{1}{z_j}\left\{\Delta F^{\circ}_{j}(\mathrm{T}) - \Delta F^{\circ}_{j}(298)\right\} + \frac{1}{z_i}\left\{\alpha^{\circ}_{i}(\mathrm{T}) - \alpha^{\circ}_{i,aq}(298)\right\} - \frac{1}{z_j}\left\{\alpha^{\circ}_{j}(\mathrm{T}) - \alpha^{\circ}_{j,aq}(298)\right\}. \tag{6}$$

Therefore we have an expression for $\alpha^{\circ}_{i}(\mathrm{T})$ from Eq. (6)

$$-\frac{1}{z_i}\alpha^{\circ}_{i}(\mathrm{T}) = \boldsymbol{a}_{ij} + \boldsymbol{b}_{ij} - \frac{1}{z_j}\alpha^{\circ}_{j}(\mathrm{T}), \tag{7}$$

where

$$\boldsymbol{a}_{ij} = \frac{1}{z_j}\alpha^{\circ}_{j,aq}(298) - \frac{1}{z_i}\alpha^{\circ}_{i,aq}(298) - \mathrm{F}\Delta \mathrm{E}^{\circ}_{ij} \tag{8}$$

$$\boldsymbol{b}_{ij} = \frac{1}{z_i}\left\{\Delta F^{\circ}_{i}(\mathrm{T}) - \Delta F^{\circ}_{i}(298)\right\} - \frac{1}{z_j}\left\{\Delta F^{\circ}_{j}(\mathrm{T}) - \Delta F^{\circ}_{j}(298)\right\} \tag{9}$$

The quantity $\boldsymbol{b}_{ij}$ which is composed of the difference in the temperature dependence of ΔF°_{i} and ΔF°_{j} may resonably be neglected within an accuracy of a few tenth volts. Then $\boldsymbol{a}_{ij}$ can be regarded as the standard molal real free energy of solvation of the ion $\mathrm{M}^{z_i}_{i}$ in the fused salt which is referred to that of the reference ion $\mathrm{M}^{z_j}_{j}$ at the given temperature, as seen from Eq. (7). On the other hand, $\boldsymbol{a}_{ij}$ is given by the algebraic sum of the free energies of hydration of the ions $\mathrm{M}^{z_i}_{i}$ and $\mathrm{M}^{z_j}_{j}$ at 25°C and the difference between the standard electrode potentials in fused salt at T and that in water at 25°C which are all known quantities, as seen from Eq. (8). In this way we can estimate $\boldsymbol{a}_{ij}$ as a function of $\alpha^{\circ}_{i,aq}(298)$ according to Eq. (8).

In the present work the $\boldsymbol{a}_{ij}$ vs. $\alpha^{\circ}_{i,aq}(298)$ plots will be shown in some fused salts for which the standard electrode potentials are available.

The standard potentials in molality scale in fused salts are quoted from the tables of Plambeck[2] and those in aqueous solutions are quoted from the tables by Dobos[3] and by Weast.[4] The redox system Ag^+/Ag or Zn^{2+}/Zn is used as the reference electrode in these fused salts. The values of $\boldsymbol{a}_{ij}$ are calculated using the values of $\alpha^{\circ}_{i,aq}(298)$ estimated by one of the authors.[5]

The values of $\boldsymbol{a}_{ij}(T)$ calculated in this way are plotted against the values of $-\frac{1}{z_i}\alpha^{\circ}_{i,aq}(298)$ in Figs. (1)-(10). In these Figures the position of $-\frac{1}{z_j}\alpha^{\circ}_{j}(T)$ for the reference ion Ag^+ or Zn^{2+} on the $\boldsymbol{a}_{ij}$-axis are chozen arbitrarily and the value of $\boldsymbol{a}_{ij}$ for an ion is measured from this position. It should be kept in mind that the values of $\boldsymbol{a}_{ij}$ are those obtained at a given temperature T, while the values of $\alpha^{\circ}_{i,aq}(298)$ are those at 25°C in all diagrams.

It is surprising that there exists a linear relation between $\boldsymbol{a}_{ij}$ and $-\frac{1}{z_i}\alpha^{\circ}_{i,aq}$ in every fused salt as in the case of non-aqueous solvents.[1]

The linear relation in the fused salts in these diagrams can be expressed by the equation

$$\boldsymbol{a}_{ij}=\boldsymbol{a}_0+\beta x\,, \tag{10}$$

TABLE. The molal real free energies of solvation $\boldsymbol{a}_0$ of the reference ions Ag^+ and Zn^{2+} in fused salts, the proportionality constant β in $-\frac{1}{z_i}\alpha^{\circ}_{i}(T)=\beta x$ and the standard deviation $\pm\sigma$ from the proportionality relation

Reference Ion	Fused salt	Temp. (K)	$-\boldsymbol{a}_0$ (ev)	β	$\pm\sigma$
Ag^+	$LiCl$-KCl	723	5.50	0.970	0.36
Ag^+	$MgCl_2$-$NaCl$-KCl	748	5.11	0.937	0.28
Ag^+	$AlCl_3$-$NaCl$-KCl	423	5.53	0.957	0.41
Ag^+	$LiNO_3$-KNO_3	450	4.86	0.997	0.04
Ag^+	$NaNO_3$-KNO_3	523	5.18	0.968	0.16
Ag^+	Li_2SO_4-K_2SO_4	898	5.45	1.035	0.33
Ag^+	$NaSCN$-$KSCN$	435	4.80	0.911	0.34
Zn^{2+}	CH_3COOLi-CH_3COONa-CH_3COOK	495	10.64	1.013	0.03
Ag^+	$NaPO_3$-KPO_3	973	4.51	0.923	0.06
Ag^+	Li_2CO_3-Na_2CO_3	823	4.82	0.972	0.02

with an accuracy of a few tenth volts, where $\boldsymbol{a}_0$ and β are constants characteristic to the solvent and x stands for $-\frac{1}{z_i}\alpha^\circ_{i,aq}(298)$.

It can be seen from Eqs. (7) and (10) that $\boldsymbol{a}_0$ equals $\frac{1}{z_j}\alpha^\circ_j(T)$ for the ion associated with the reference redox system, since $\alpha^\circ_i(T)$ can be regarded as equal to zero at x=0 as discussed in the previous work.[1] In this way we have a proportionality relation between $-\frac{1}{z_i}\alpha^\circ_i(T)$ and x from Eq. (7)

$$-\frac{1}{z_i}\alpha^\circ_i(T)=\boldsymbol{a}_{ij}-\boldsymbol{a}_0=\beta x\,, \tag{11}$$

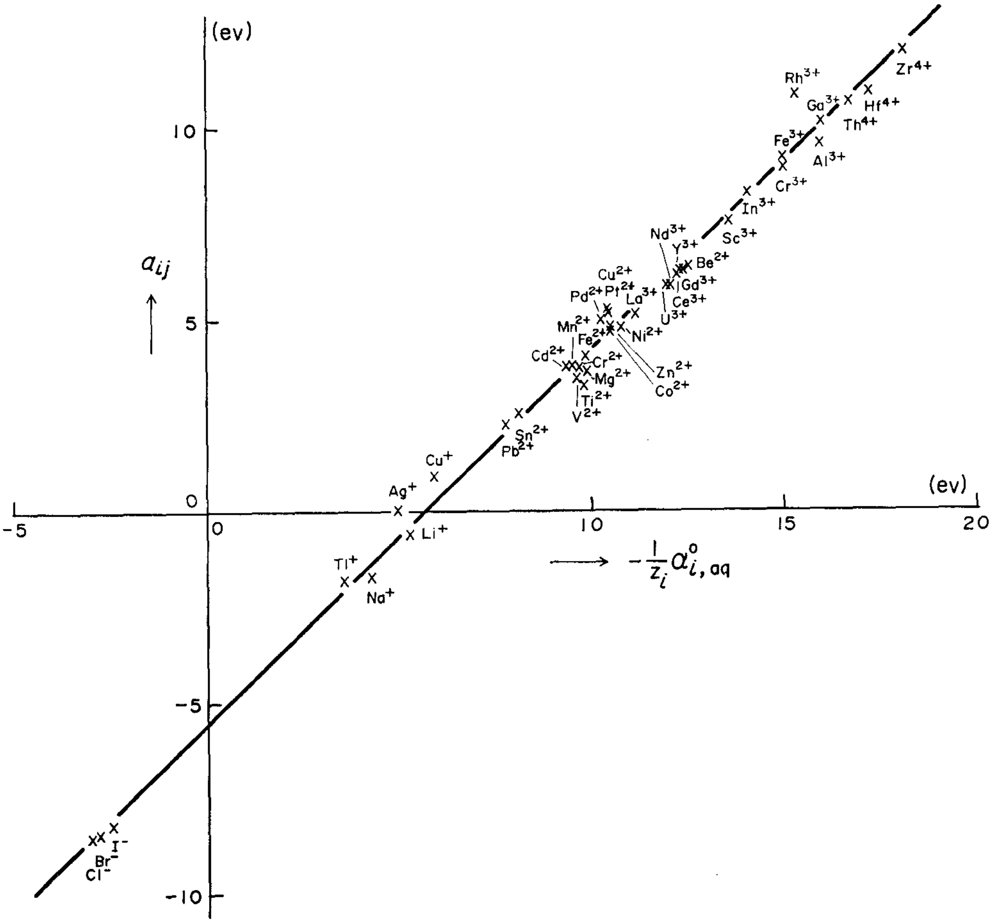

Fig. 1. $\alpha_{ij}(T)$ vs. $-\frac{1}{z_i}\alpha^\circ_{i,aq}(298)$ in LiCl-KCl at 450°C.

within an accuracy of neglecting $\boldsymbol{b}_{ij}$.

The values of $\boldsymbol{a}_0$ and β are listed in the Table for a series of fused salts. As seen from the Table, the values of β are quite close to unity.

Although the value of $-\frac{1}{z_i}\alpha_i^o(T)$ estimated by Eq. (11) includes an uncertainty of a few tenth volts, it may be sure to conclude from these diagrams that the free energies of solvation of monoatomic ions in fused salts are proportional to those of hydration with the coefficient close to unity as in the case of solvation in non-aqueous solvents.[1] Therefore it is suggested that the formation of the solvation bonding of monoatomic ions should be explained by some similar mechanism in water, non-aqueous sol-

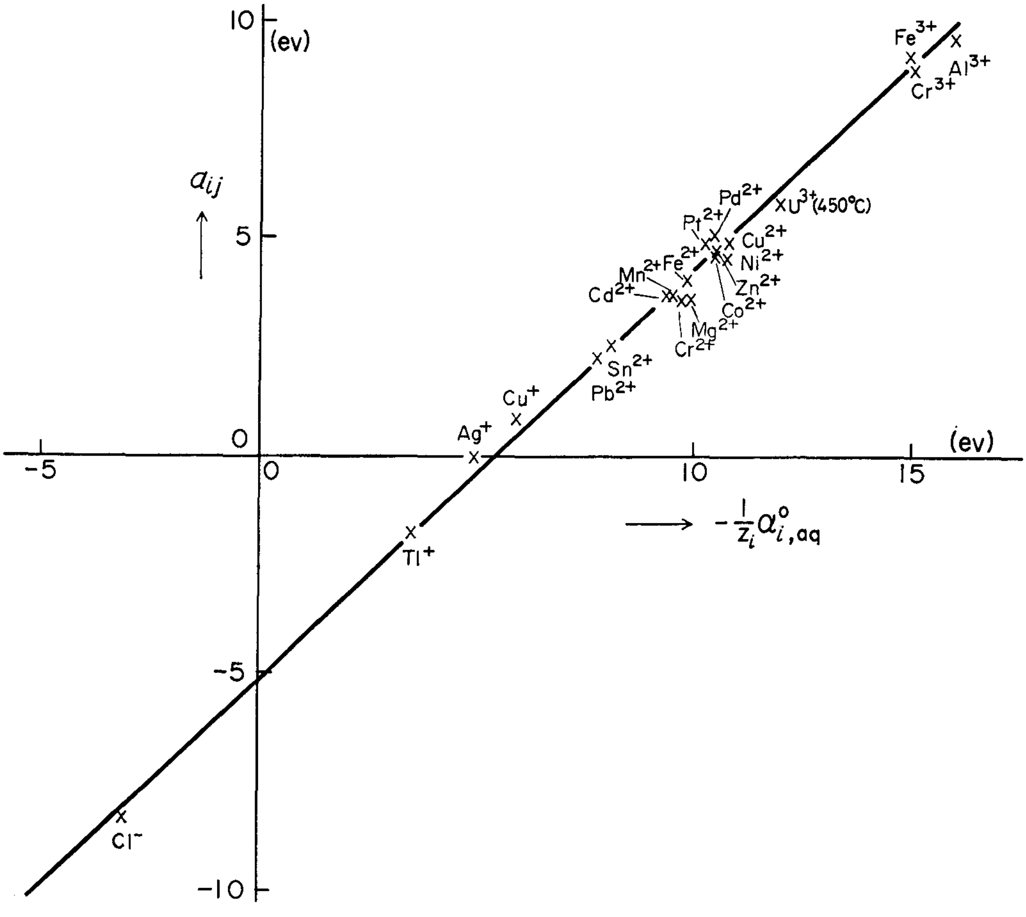

Fig. 2. $a_{ij}(T)$ vs. $-\frac{1}{z_i}\alpha^o_{i,aq}(298)$ in $MgCl_2$-NaCl-KCl at 475°C.

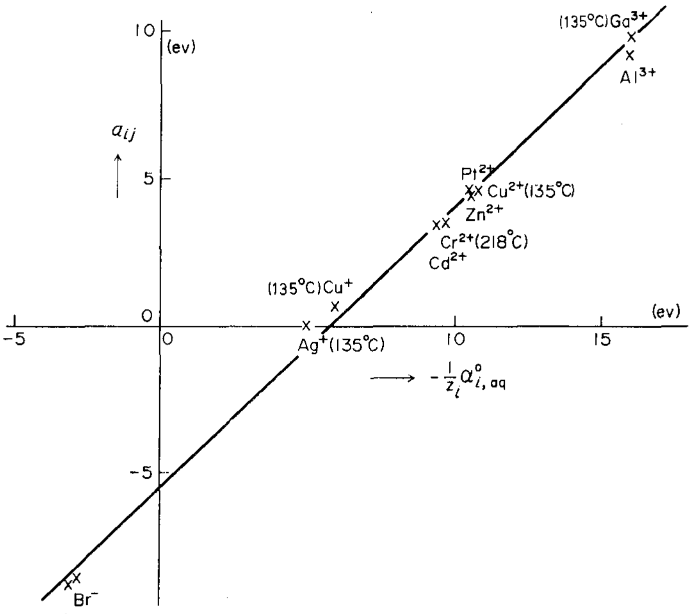

Fig. 3. $a_{ij}(T)$ vs. $-\frac{1}{z_i}\alpha^0_{i,aq}(298)$ in $AlCl_3$-NaCl-KCl at 150°C.

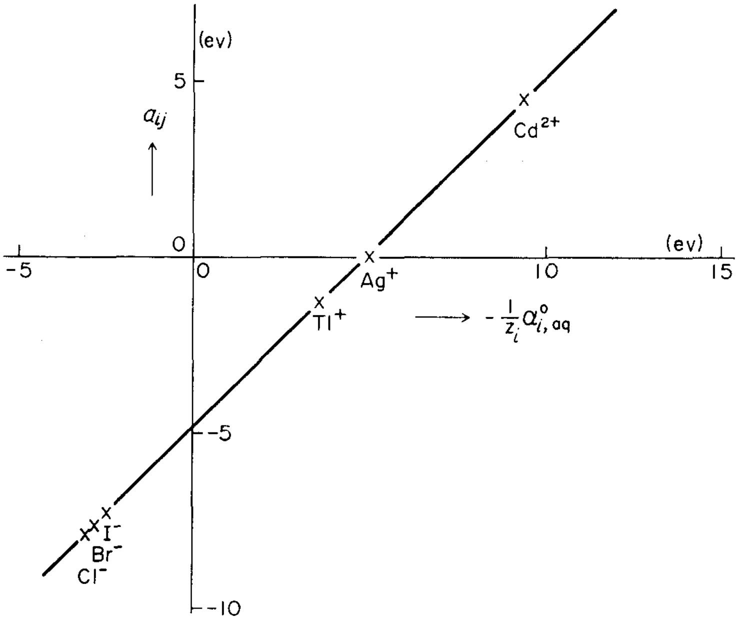

Fig. 4. $a_{ij}(T)$ vs. $-\frac{1}{z_i}\alpha^0_{i,aq}$ in $LiNO_3$-KNO_3 at 177°C.

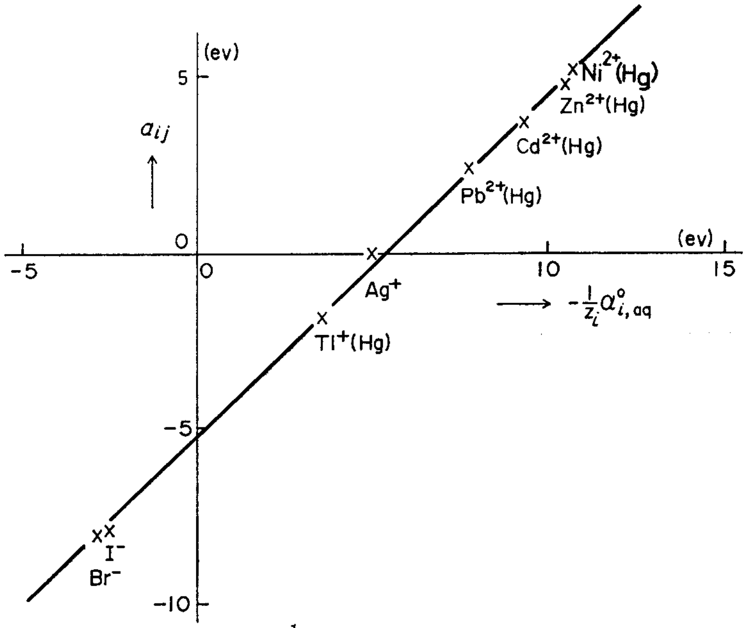

Fig. 5. $a_{ij}(T)$ vs. $-\frac{1}{z_i}\alpha^\circ_{i,aq}(298)$ in $NaNO_3$-KNO_3 at 250°C.

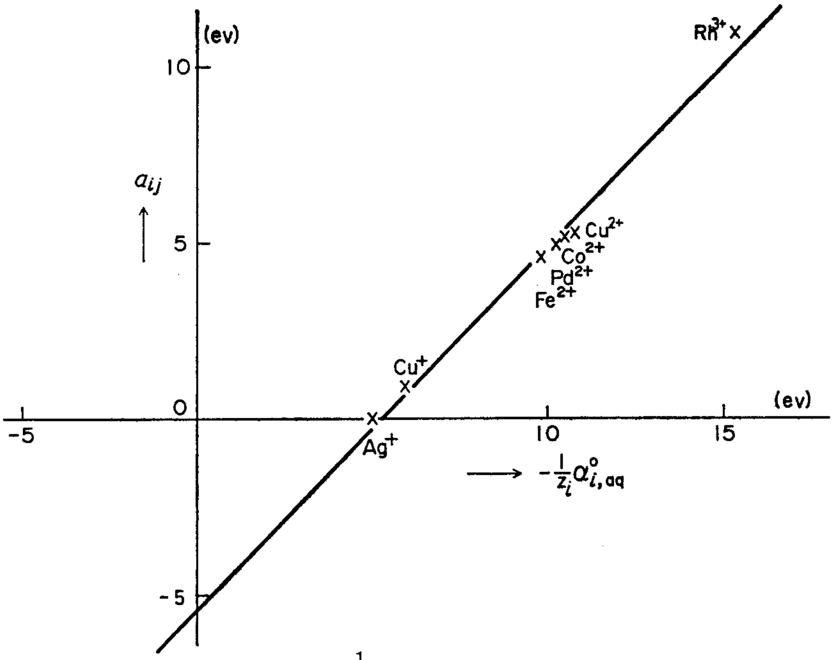

Fig. 6. $a_{ij}(T)$ vs. $-\frac{1}{z_i}\alpha^\circ_{i,aq}$ in Li_2SO_4-K_2SO_4 at 625°C.

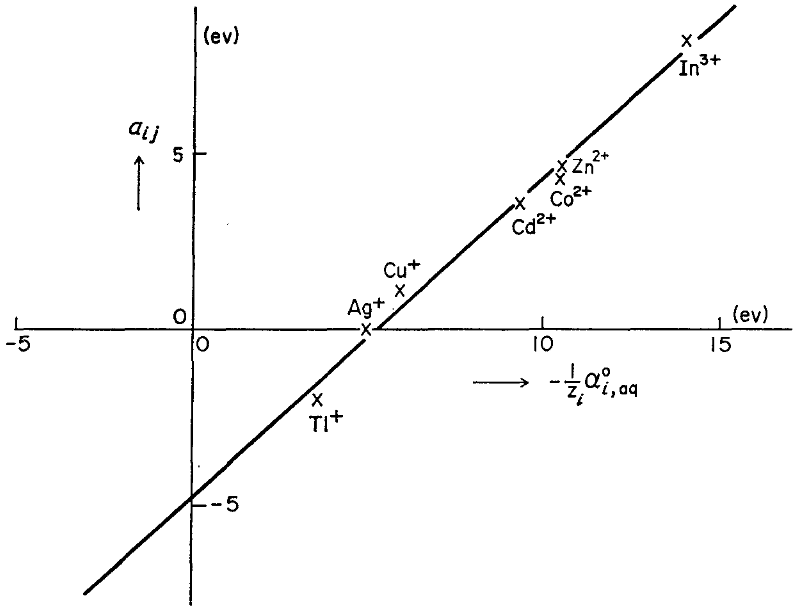

Fig. 7. $a_{ij}(T)$ vs. $-\frac{1}{z_i}\alpha^{\circ}_{i,aq}(298)$ in NaSCN-KSCN at 161.85°C.

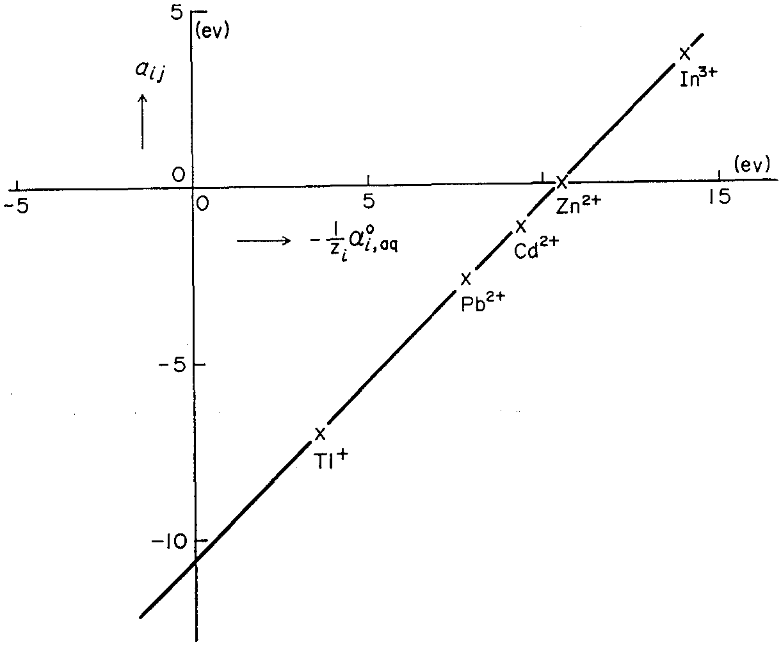

Fig. 8. $a_{ij}(T)$ vs. $-\frac{1}{z_i}\alpha^{\circ}_{i,aq}(298)$ in CH_3COOLi-CH_3COONa-CH_3COOK at 221.85°C.

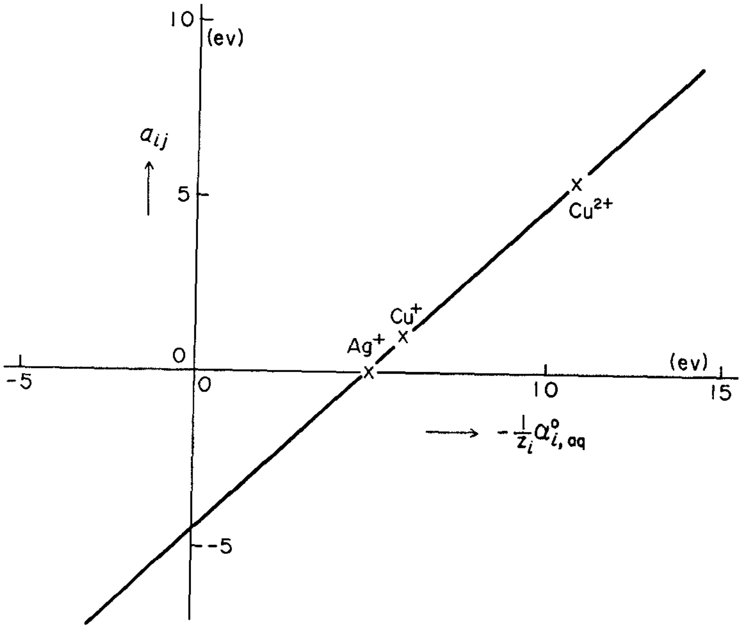

Fig. 9. a_{ij}(T) vs. $-\frac{1}{z_i}\alpha^{\circ}_{i,aq}$(298)in NaPO$_3$-KPO$_3$ at 700°C.

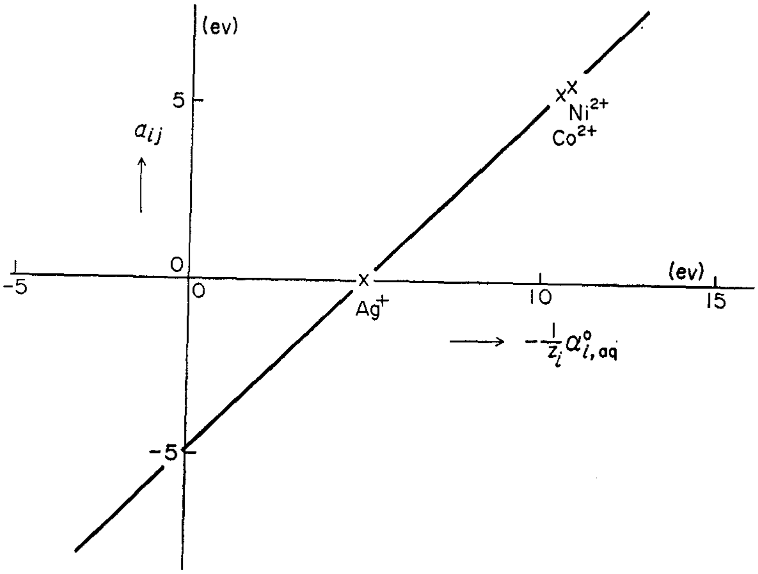

Fig. 10. a_{ij}(T) vs. $-\frac{1}{z_i}\alpha^{\circ}_{i,aq}$(298) in Li$_2CO_3$-Na$_2CO_3$ at 550°C.

vents and also in fused salts.

The values of $-\frac{1}{z_i}\alpha_i^\circ(\mathrm{T})$ will be discussed in a later paper in detail taking into account the temperature dependence of ΔF_i° which is neglected in the present treatments.

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