

VERIFICATION OF ACCURACY OF STANDARD THERMODYNAMIC DATA OF INORGANIC ELECTROLYTES

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Accuracy of standard thermodynamic data for some inorganic electrolytes of the types 1-1, 1-2 and 2-1 at 25 °C, in the solid state or aqueous standard solutions, presented in NBS Tables (1982), has been checked. For the purpose, the condition for the pure solid-saturated solution equilibrium and reliable values of solubilities, mean activity coefficients and water activity in saturated solution at the given temperature were used. In most cases, a very good reliability and consistency of all relevant data have been found. On the other hand, some discrepancies have been observed for NaNO_3 , $\text{NaClO}_4/\text{NaClO}_4$ pair, $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}/\text{Na}_2\text{HPO}_4$ pair, K_2CrO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, $(\text{NH}_4)_2\text{SO}_4$ and $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}/\text{SrCl}_2$ pair the reason of which is not yet known. The verification method can be used for the determination of lacking thermodynamic data. The method has been applied to $\Delta G_{\text{f,cr}}^\circ$ of $\text{NaCNS} \cdot 2\text{H}_2\text{O}$, $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$, $\text{Na}_2\text{CrO}_4 \cdot 6\text{H}_2\text{O}$, $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, $\text{MgI}_2 \cdot 8\text{H}_2\text{O}$ and $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ at 25 °C. A suitable method has been used for the determination of the most probable solubility in the case when the values scatter. The used methods are applicable to all types of electrolytes and nonelectrolytes.

Keywords: Standard thermodynamic data; Inorganic electrolytes; Accuracy; Verification.

So far, the most comprehensive and reliable data for the standard thermodynamic properties of inorganic and some organic substances, in the solid state and standard aqueous solution at 25 °C, have been presented in *NBS Tables of Chemical Thermodynamic Properties*¹. The reliability of the data is described "...the overall uncertainty lies between 8 and 80 units of the last (right-most) digit...". In a study on the estimation of missing standard thermodynamic data for solid alkali metal and ammonium peroxodisulfates², a common method for checking the reliability of the estimated values of $\Delta G_{\text{f,cr}}^\circ$ has been used, based on the condition for the equilibrium of solid pure substance and its saturated solution, at the given temperature. In the case of the peroxodisulfates, the required data were not yet known. The method was first checked for selected groups of electrolytes of the types 1-1, 1-2 and 2-1. The preliminary treatment of some electrolytes has shown that besides the cases with the reliability of the published data correspond-

ing to the above given statement, also cases with surprising discrepancies have been detected. Therefore, the aim of this contribution is the verification of the accuracy and consistency of published standard thermodynamic data on inorganic electrolytes of the above given types¹ with all required data known with sufficient reliability.

RESULTS AND DISCUSSION

The thermodynamic condition of the equilibrium between a solid electrolyte $C_cA_a \cdot nH_2O$ (C and A represent cation and anion, c , a and n are stoichiometric numbers) and its saturated solution is expressed by the relationship

$$\Delta G_{f,cr}^{\circ}(C_cA_a \cdot nH_2O) = \Delta G_{f,aq}^{\circ}(C_cA_a) + n\Delta G_{f,l}^{\circ}(H_2O,l) + RT \ln(m_{C,sat}^c m_{A,sat}^a \gamma_{sat}^v a_{w,sat}^n) \quad (1)$$

where $\Delta G_{f,cr}^{\circ}(C_cA_a \cdot nH_2O)$ represents the standard Gibbs energy of formation of the considered solid electrolyte, $\Delta G_{f,aq}^{\circ}(C_cA_a)$ denotes the standard Gibbs energy of formation of the considered anhydrous electrolyte in its aqueous standard state, $m_{C,sat}$ and $m_{A,sat}$ denote the molality of cation C and anion A in the saturated solution related to 1 kg of total water; $v = c + a$, γ_{sat} represents the mean activity coefficient and $a_{w,sat}$ the water activity in the saturated solution. In an ideal case, when values of all measured quantities are absolutely correct, then the value of quantity Φ

$$\Phi = \Delta G_{f,cr}^{\circ}(C_cA_a \cdot nH_2O) - \Delta G_{f,aq}^{\circ}(C_cA_a) - n\Delta G_{f,l}^{\circ}(H_2O,l) \quad (2)$$

and quantity Ψ

$$\Psi = RT \ln(m_{C,sat}^c m_{A,sat}^a \gamma_{sat}^v a_{w,sat}^n) \quad (3)$$

must be equal, and their difference $\Delta = \Phi - \Psi = 0$. In reality, however, all data of considered quantities have been mostly obtained with some uncertainty which causes that $\Delta \neq 0$. As any information about the values of Δ of individual substances has been missing in the literature so far, the aim of this contribution is therefore to calculate values of the difference Δ for selected groups of inorganic electrolytes of the type 1-1, 1-2 and 2-1 with known and sufficiently reliable values of all quantities present in Eq. (1). The values of $\Delta G_{f,cr}^{\circ}(C_cA_a \cdot nH_2O)$ and $\Delta G_{f,aq}^{\circ}(C_cA_a)$ (in kJ mol^{-1}) were taken from ref.¹, solubility data mostly from refs³⁻⁷, the mean activity coefficients of saturated solutions were taken or calculated from corresponding relationships for 1-1 electrolytes from ref.⁴, for 1-2 electrolytes from ref.⁵ (for

$(\text{NH}_4)_2\text{SO}_4$ from ref.⁶) and for 2-1 electrolytes from ref.⁷ Water activities of saturated solutions were similarly taken from the published data or calculated from corresponding osmotic coefficients of saturated solutions ϕ_s (refs⁴⁻⁷). For the calculations, the value of $\Delta G_f^\circ(\text{H}_2\text{O}, \text{l}) = -237.129 \text{ kJ mol}^{-1}$ has been taken from ref.¹ The results of the treatment are summarized in Table I. The values of the quantity Φ calculated from Eq. (2) are not given in the table.

As can be seen from Table I, in most of the cases when the activity coefficients have been measured up to the saturation concentration, the absolute value $|\Delta| < 0.08 \text{ kJ mol}^{-1}$ and in most of the other cases $|\Delta| < 0.8 \text{ kJ mol}^{-1}$. This conclusion can be considered as verification of sufficient accuracy and consistency of the tabulated values of standard formation energies of the considered substances¹ on one hand and corresponding data on their solubility, mean activity coefficients and water activities of saturated solutions taken from other sources³⁻⁷ on the other hand. Small differences in solubility data of ref.³ and refs⁴⁻⁷ had no substantial effect on the results. Absolute values $|\Delta| > 1 \text{ kJ mol}^{-1}$, however, suggest some inconsistency between individual relevant quantities, i.e., some of these values are more or less incorrect. In this study, this concerns the $\text{NaClO}_4 \cdot \text{H}_2\text{O}/\text{NaClO}_4$ pair, NaNO_3 , $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}/\text{Na}_2\text{HPO}_4$ pair, KH_2AsO_4 , K_2CrO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, CsI , $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}/\text{Na}_2\text{SO}_3$ pair, $(\text{NH}_4)_2\text{SO}_4$, and $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}/\text{SrCl}_2$ pairs. In the cases of KH_2AsO_4 and CsI , the obtained absolute values $|\Delta| = 1.3\text{--}2.6 \text{ kJ mol}^{-1}$ were most probably caused by an inappropriate extrapolation in calculation of mean activity coefficients to the saturation concentration, which is higher than the highest measured concentration. For the same reason, the proposed verification method could not be used for the other substances in refs^{4,5,7}, LiI , NaClO_3 , NaH_2AsO_4 , RbF , CsF , K_2HPO_4 , K_2HAsO_4 , Cs_2SO_4 , CaI_2 , SrI_2 and BaI_2 . On the other hand, in the case of $\text{BaBr}_2 \cdot 2\text{H}_2\text{O}$, an almost negligible value of $\Delta = -0.031 \text{ kJ mol}^{-1}$ has been obtained even if an expression derived for $m \leq 2.321 \text{ mol kg}^{-1}$ for calculation of the activity coefficient at $m_s = 3.3595 \text{ mol kg}^{-1}$ has been used. In the case of NaNO_3 , $\text{K}_2\text{Cr}_2\text{O}_7$ and $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}/\text{SrCl}_2$ pair, however, the obtained quite high values of $|\Delta| > 3 \text{ kJ mol}^{-1}$ are very surprising because in these cases the mean activity coefficients and osmotic coefficients have been measured up to the saturation concentrations. Any detailed elucidation of these discrepancies was not the subject of this contribution, but they deserve an appropriate attention of specialists dealing with these substances.

From the obtained results, however, another conclusion can be derived: in the cases, when the values of $\Delta G_{f,\text{aq}}^\circ(\text{C}_c\text{A}_a)$, m_{sat} , γ_{sat} and $a_{\text{w,sat}}$ are known

TABLE I
The difference Δ for selected electrolytes of the type 1-1, 1-2 and 2-1 at 25 °C^a

Substance	$-\Delta G_{f,cr}^{\circ}$ kJ mol ⁻¹	$-\Delta G_{f,aq}^{\circ}$ kJ mol ⁻¹	m_{sat} mol kg ⁻¹	γ_{sat}	$a_{w,sat}$	Ψ kJ mol ⁻¹	Δ kJ mol ⁻¹
Type 1-1							
LiCl·H ₂ O	631.80	424.58	19.219 ^b	58.4 ^b	0.1186 ^b	-29.536	-0.373
			19.966	62.19 ^f	0.1090 ^f	-29.827	-0.082
LiBr·2H ₂ O	840.5	397.27	20.698	557 ^e	0.0427 ^e	-30.734	-0.266
LiClO ₄ ·3H ₂ O	1001.00	302.0	5.513	3.529	0.6739 ^e	11.781	0.606
LiNO ₃ ·3H ₂ O	1103.5	404.5	12.431	3.212 ^f	0.456 ^f	12.440	-0.053
NaF	543.494	540.68	0.983 ^b	0.574 ^b	-	-2.837	0.023
NaCl	384.138	393.133	6.144 ^b	1.004 ^b	-	9.021	-0.026
			6.153	1.005 ^f	-	9.033	-0.038
NaBr·2H ₂ O	828.29	365.849	9.191	2.001 ^e	0.5825 ^e	11.757	0.060
NaI·2H ₂ O	771.10	313.47	12.274	6.038 ^e	0.381 ^e	16.562	0.066
NaClO ₄ ·H ₂ O	494.29	270.41	17.208	1.007 ^f	0.406 ^f	11.907	1.342
NaBrO ₃	242.62	243.29	2.617 ^b	0.421 ^b	-	0.480	0.190
			2.597	0.423 ^f	-	0.466	0.204
NaNO ₃	367.00	373.15	10.830 ^b	0.641 ^b	-	9.606	-3.456
			10.723	0.617 ^f	-	9.368	-3.218
KF·2H ₂ O	1021.49	562.06	17.359	3.763 ^f	0.3076 ^f	14.87	-0.047
KCl	409.14	414.49	4.803 ^b	0.589 ^b	-	5.156	0.194
			4.787	0.589 ^e	-	5.139	0.211
KBr	380.66	387.23	5.702	0.641 ^e	-	6.426	0.144
KI	324.892	334.85	8.928	0.825 ^e	-	9.900	0.058
KClO ₃	296.25	291.22	0.7017	0.519 ^e	-	-5.008	-0.022
KBrO ₃	271.16	264.67	0.4874	0.556 ^e	-	-6.473	-0.017
KNO ₃	394.86	394.53	3.7892	0.236 ^e	-	-0.554	0.224
KH ₂ PO ₄	1415.85	1413.55	1.8239	0.329 ^e	-	-2.532	0.232
KH ₂ AsO ₄	1035.9	1036.45	1.6914	0.392 ^e	-	-2.037	2.587
RbCl	407.80	415.20	7.7174	0.570 ^f	-	7.344	0.056
RbBr	381.79	387.94	7.038	0.525 ^e	-	6.480	-0.330
RbI	328.86	335.56	7.767	0.535 ^e	-	7.062	-0.362
RbNO ₃	395.78	395.24	4.415	0.204 ^e	-	-0.519	-0.021
CsCl	414.53	423.24	11.401	0.513 ^e	-	8.757	-0.047
CsBr	391.41	395.97	5.807	0.451 ^e	-	4.773	-0.213
CsI	340.58	343.59	3.271	0.426 ^e	-	1.645	1.365

TABLE I
(Continued)

Substance	$-\Delta G_{f,cr}^{\circ}$ kJ mol ⁻¹	$-\Delta G_{f,aq}^{\circ}$ kJ mol ⁻¹	m_{sat} mol kg ⁻¹	γ_{sat}	$a_{w,sat}$	Ψ kJ mol ⁻¹	Δ kJ mol ⁻¹
CsNO ₃	406.54	403.27	1.427	0.366 ^f	–	-3.220	-0.050
NH ₄ Cl	202.87	210.52	7.405 ^b	0.565 ^b	–	7.096	0.554
			7.330	0.565 ^f	–	7.045	0.605
NH ₄ ClO ₄	88.75	87.83	2.100 ^b	0.394 ^b	–	-0.939	0.019
			2.097	0.394 ^f	–	-0.946	0.026
NH ₄ NO ₃	183.87	190.56	25.954 ^a	0.131 ^a	–	6.067	0.623
			26.496	0.129 ^e	–	6.094	0.596
AgNO ₃	33.41	34.16	13.821	0.087 ^f	–	0.914	-0.164
Type 1-2							
Li ₂ SO ₄ ·H ₂ O	1565.5	1331.20	3.140 ^c	0.2993 ^c	0.8435 ^c	2.553	0.276
Na ₂ SO ₄ ·10H ₂ O	3646.85	1268.36	1.957 ^c	0.1558 ^c	0.9360 ^c	-7.036	-0.164
			1.9621	0.1556 ^g	0.9359 ^g	-7.030	-0.170
Na ₂ SO ₃ ·7H ₂ O	2676.1	1010.39	2.438	0.1923 ^g	0.9055 ^g	-3.920	-1.887
Na ₂ S ₂ O ₃ ·5H ₂ O	2229.8	1046.0	4.797	0.2682 ^g	0.7451 ^g	1.663	0.182
Na ₂ CO ₃ ·10H ₂ O	3427.66	1051.64	2.767 ^c	0.1721 ^c	0.8977 ^c	-4.756	0.026
			2.788	0.1720 ^h	0.8968 ^h	-4.730	0.000
Na ₂ HPO ₄ ·12H ₂ O	4467.8	1612.98	0.8254	0.2107 ^h	0.9728 ^h	-10.392	1.120
K ₂ SO ₄	1321.37	1311.07	0.692 ^c	0.2237 ^c	–	-10.438	0.138
			0.688	0.2242 ^h	–	-10.464	0.164
K ₂ CrO ₄	1295.7	1294.3	3.3416	0.1934 ^h	–	0.190	-1.590
K ₂ Cr ₂ O ₇	1881.8	1867.6	0.507 ^c	0.4342 ^c	–	-7.819	-6.381
			0.5129	0.4320 ^e	–	-7.771	-6.429
Rb ₂ SO ₄	1316.89	1312.50	1.9012	0.1800 ^h	–	-4.538	0.148
(NH ₄) ₂ SO ₄	901.67	903.145	5.843 ^k	0.112 ^k	–	0.283	1.192

TABLE I
 (Continued)

Substance	$-\Delta G_{f,cr}^0$ kJ mol ⁻¹	$-\Delta G_{f,aq}^0$ kJ mol ⁻¹	m_{sat} mol kg ⁻¹	γ_{sat}	$a_{w,sat}$	Ψ kJ mol ⁻¹	Δ kJ mol ⁻¹
	Type 2-1						
MgCl ₂ ·6H ₂ O	2114.64	717.1	5.781	30.805 ^j	0.3391 ^j	25.891	-0.657
MgBr ₂ ·6H ₂ O	2055.7	662.7	5.610 ^d 5.558	70.166 ^d 66.262 ^j	0.3104 ^d 0.3166 ^j	30.474 30.273	-0.700 -0.499
CaBr ₂ ·6H ₂ O	2152.8	761.49	7.660 ^d 7.624	285.193 ^d 276.895 ^j	0.1433 ^d 0.1454 ^j	31.723 31.685	-0.259 -0.221
SrCl ₂ ·6H ₂ O	2240.92	821.91	3.518 ^d 3.5046	1.456 ^d 1.445 ^j	0.7099 ^d 0.7115 ^j	10.489 0.438	-6.725 -6.674
BaCl ₂ ·2H ₂ O	1296.32	823.21	1.785 ^d 1.774	0.4417 ^d 0.4409 ^j	0.9028 ^d 0.9037 ^j	1.162 1.109	-0.014 0.039
BaBr ₂ ·2H ₂ O	1230.4	768.68	3.3595	1.2075 ^j	0.7722 ^j	12.569	-0.031

^a Solubility data without index after ref.³; ^b ref.⁴; ^c ref.⁵; ^d ref.⁷; ^e admissible extrapolation after ref.⁴; ^f calculation after ref.⁴; ^g admissible extrapolation after ref.⁵; ^h calculation after ref.⁵; ^j calculation after ref.⁷; ^k ref.⁶

with a sufficiently high accuracy, then a lacking value of $\Delta G_{f,cr}^0(C_c A_a \cdot nH_2O)$ of the considered solid substance coexisting with its saturated solution at a given temperature can be calculated using Eq. (1). Combining Eqs (1) and (3) it follows that

$$\Delta G_{f,cr}^0(C_c A_a \cdot nH_2O) = \Delta G_{f,aq}^0(C_c A_a) + n\Delta G_f^0(H_2O,l) + \Psi \quad (4)$$

This procedure has been used for some substances of the considered types for which no values of $\Delta G_{f,cr}^0$ are given in the NBS Tables¹, for which, however, sufficiently accurate values of other necessary quantities are available. The results of this procedure applied to the calculation of $\Delta G_{f,cr}^0$ of NaSCN·2H₂O, NaH₂PO₄·2H₂O, Na₂CrO₄·6H₂O, Na₂WO₄·2H₂O, MgI₂·8H₂O and CaCl₂·6H₂O are presented in Table II.

As can be seen from the table, the obtained values of $\Delta G_{f,cr}^0$ of a given substance differ almost negligibly, even though some differences exist in solubility values and therefore also in activity coefficient and water activity values of saturated solutions. The same applies to different evaluation pro-

cedures used for the calculation of γ_s and $a_{w,s}$ for the same solubility values. This conclusion can be best shown on the results for $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ with quite different solubility data in the range 7.29–7.639 mol kg^{-1} (refs.^{3,7,8a}) using the published evaluation procedures^{7,9}. The average value of $\Psi_{\text{sat}} = 22.528$ kJ mol^{-1} led to the following value of $\Delta G_{\text{f}}^{\circ}(\text{CaCl}_2 \cdot 6\text{H}_2\text{O}) = -2216.256$ kJ mol^{-1} . The sufficiently high reliability of this result can be documented by a good agreement with the corresponding value -2215.66 ± 0.5 kJ mol^{-1} calculated using another treatment^{8a,8b}. Here, the total difference of 0.596 kJ mol^{-1} must be predominantly ascribed to different values¹⁰ of $\Delta G_{\text{f}}^{\circ}(\text{CaCl}_2, \text{aq}) = -815.24$ kJ mol^{-1} and $\Delta G_{\text{f}}^{\circ}(\text{H}_2\text{O}, \text{l}) = -237.190$ kJ mol^{-1} used in ref.^{8a} instead of -816.01 kJ mol^{-1} and -237.129 kJ mol^{-1} (ref.¹) used in the present contribution. The use of those values¹⁰ together with the present value of Ψ led to $\Delta G_{\text{f}}^{\circ}(\text{CaCl}_2 \cdot 6\text{H}_2\text{O}) = -2215.856$ kJ mol^{-1} which agrees even better with the value obtained by Pitzer^{8a}.

The quite great scatter of solubility data for CaCl_2 at 25 °C (7.29–7.63 mol kg^{-1}) can be explained by a great ability of this substance to form supersaturated solutions. From the measurements of osmotic and activity coefficients of aqueous solutions of this substance at 25 °C evaluated up to $m = 9.000$ mol kg^{-1}

TABLE II
Values of $\Delta G_{\text{f,cr}}^{\circ}$ of some electrolytes of the type 1-1, 1-2 and 2-1 according to Eq. (5)

Substance	$-\Delta G_{\text{f,aq}}^{\circ}$ kJ mol^{-1}	m_{sat} mol kg^{-1}	γ_{sat}	$a_{w,\text{sat}}$	Ψ kJ mol^{-1}	$-\Delta G_{\text{f,cr}}^{\circ}$ kJ mol^{-1}	
NaSCN·2H ₂ O	169.18	17.589 ^a	3.237 ^g	0.3473 ^g	14.7968	628.64	
		18.692 ^b	3.071 ^g	0.3420 ^g	14.7604	628.68	
NaH ₂ PO ₄ ·2H ₂ O	1392.17	7.969 ^c	0.1591 ^h	0.7019 ^h	-0.5782	1867.00	
Na ₂ CrO ₄ ·6H ₂ O	1251.58	5.2203 ^c	0.4661 ⁱ	0.6575 ⁱ	3.8127	2670.54	
Na ₂ WO ₄ ·2H ₂ O	404.5	2.523 ^d	0.3008 ^d	0.8766 ^d	0.7320	878.03	
		2.5274 ^c	0.3009 ⁱ	0.8764 ⁱ	9.7463	878.01	
MgI ₂ ·8H ₂ O	558.1	5.2656 ^c	157.444 ^k	0.2946 ^k	29.1771	2425.95	
CaCl ₂ ·6H ₂ O	816.0	7.462 ^e	21.847 ^e	0.2830 ^e	22.544	2216.24	
			21.750 ^l	0.2833 ^l	22.526	2216.26	
			7.639 ^l	23.203 ^m	0.2734 ^m	22.653	2216.13
				23.144 ^l	0.2736 ^l	22.645	2216.14
			7.29 ⁿ	20.452 ^m	0.2932 ^m	22.406	2216.38
				20.409 ^l	0.2933 ^l	22.396	2216.39

^a Ref.¹²; ^b ref.¹¹; ^c ref.³; ^d ref.⁵; ^e ref.⁷; ^g ref.⁴; ^h admissible extrapolation after ref.⁴; ⁱ admissible extrapolation after ref.⁵; ^k admissible extrapolation after ref.⁷; ^l ref.⁹; ^m ref.⁷; ⁿ ref.^{8a}

(ref.⁹) and to $m = 10.000 \text{ mol kg}^{-1}$ (ref.⁷) it followed that the Ψ values for the range $m = 7.00\text{--}10.00 \text{ mol kg}^{-1}$ at $25 \text{ }^\circ\text{C}$ show a smooth course from the unsaturated to supersaturated concentrations, without any abrupt change at the saturation, but with a distinct maximum at ca. 9.2 mol kg^{-1} (Table III).

Using the data in ref.⁷, the course of Ψ vs m can be expressed by a quadratic equation

$$\Psi = 6.9342 + 3.5124m - 0.19067m^2 \quad (5)$$

from which it followed that $\Psi_{\text{max}} = 9.2107 \text{ kJ mol}^{-1}$. The evaluation of data according to ref.⁹ for the limited range of m from 7.00 to 9.00 mol kg^{-1} led to the quadratic equation

TABLE III
Dependence of Ψ vs m of CaCl_2 solutions at $25 \text{ }^\circ\text{C}$

m mol kg^{-1}	γ	a_w	Ψ
7.000	18.215 ^a	0.3115 ^a	22.143 ^a
	18.17 ^b	0.3117 ^b	22.135 ^b
7.250	20.181 ^a	0.2954 ^a	22.377 ^a
7.462	21.847 ^a	0.2830 ^a	22.544 ^a
7.500	22.148 ^a	0.2808 ^a	22.567 ^a
	22.05 ^b	0.2812 ^b	22.555 ^b
7.750	24.132 ^a	0.2674 ^a	22.722 ^a
8.000	26.111 ^a	0.2551 ^a	22.844 ^a
	26.04 ^b	0.2553 ^b	22.835 ^b
8.250	28.09 ^a	0.2438 ^a	22.942 ^a
8.500	30.07 ^a	0.2332 ^a	23.009 ^a
	30.17 ^b	0.2327 ^b	23.002 ^b
8.750	32.07 ^a	0.2233 ^a	23.059 ^a
9.000	34.11 ^a	0.2138 ^a	23.080 ^a
	34.20 ^b	0.2135 ^b	23.079 ^b
9.250	36.23 ^a	0.2048 ^a	23.093 ^a
9.500	38.43 ^a	0.1961 ^a	23.084 ^a
9.750	40.73 ^a	0.1877 ^a	23.058 ^a
10.000	43.12 ^a	0.1796 ^a	23.014 ^a

^a Ref.⁷, ^b ref.⁹

$$\Psi = 2.4919 + 4.6441m - 0.26257m^2 \quad (6)$$

which is quite different from Eq. (5), but it leads to almost identical values of Ψ in the corresponding concentration range. The knowledge of the Ψ vs m plot for the range of unsaturated to superstaturated solutions can be used for the calculation of the “true” value of the saturation concentration m_{sat} in cases when the experimentally determined solubility data exhibit a great scatter. For the case that the plot of Ψ vs m can be expressed by a quadratic equation, then for the saturation state Eq. (7) must be valid

$$\Psi_{\text{sat}} = \Phi = a + bm_{\text{sat}} + cm_{\text{sat}}^2 \quad (7)$$

from which it follows that

$$m_{\text{sat}} = [-b - (b^2 - 4c(a - \Psi_{\text{sat}}))^{0.5}]/(2c) . \quad (8)$$

For the case of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ with $\Psi_{\text{sat}} = 22.528 \text{ kJ mol}^{-1}$ it follows that the “true” value $m_{\text{sat}} = 7.464 \text{ mol kg}^{-1}$ (using Eq. (5)) and $m_{\text{sat}} = 7.465 \text{ mol kg}^{-1}$ (using Eq. (6)), both values mutually agreeing very well and being approximately in the middle of the experimentally determined range. The average “true” value of $m_{\text{sat}} = 7.4645 \text{ mol kg}^{-1}$ and the corresponding value of $\gamma_{\text{sat}} = 21.847$ and $a_{\text{w,sat}} = 0.2830$ led to $\Psi_{\text{sat}} = 22.547 \text{ kJ mol}^{-1}$ and, consequently, to the “true” value of $\Delta G^{\circ}_{\text{f}}(\text{CaCl}_2 \cdot 6\text{H}_2\text{O}) = -2216.237 \text{ kJ mol}^{-1}$ which is almost identical with the average value given above.

A similar smooth course of the Ψ vs m dependence could also be observed for solutions of CaBr_2 at $25 \text{ }^{\circ}\text{C}$ with osmotic and activity coefficients evaluation⁷ up to $m = 9.210 \text{ mol kg}^{-1}$ and with $m_{\text{sat}} = 7.660 \text{ mol kg}^{-1}$ (ref.⁷) or $7.624 \text{ mol kg}^{-1}$ (ref.³). For the range of m from 7.00 to 9.21 mol kg^{-1} , this course could be expressed by the equation

$$\Psi = -4.3846 + 8.1953m - 0.4547m^2 . \quad (9)$$

Using the NBS data¹ for $\Delta G^{\circ}_{\text{f}}(\text{CaBr}_2 \cdot 6\text{H}_2\text{O}) = -2152.8 \text{ kJ mol}^{-1}$ and $\Delta G^{\circ}_{\text{f}}(\text{CaBr}_2, \text{aq}) = -761.49 \text{ kJ mol}^{-1}$, the following “true” value of $m_{\text{sat}} = 7.4717 \text{ mol kg}^{-1}$ has been calculated as the more probable one. However, this value is distinctly lower than both the experimental values. This leads to the conclusion that also in this case some or all quantities determining the values Φ and Ψ deserve further refining. Any presentation of further results with similar cases with all necessary data exceeds the scope of this contri-

bution. It seems, however, that the used procedure could be very helpful with other electrolytes at which the determined value $|\Delta| > \text{ca. } 0.2 \text{ kJ mol}^{-1}$.

A comment on the results for the $\text{NaSCN}\cdot 2\text{H}_2\text{O}/\text{NaSCN}$ pair is desirable. In the original paper¹¹ on the solubility of this salt, monohydrate $\text{NaSCN}\cdot\text{H}_2\text{O}$ has been given as the solid phase coexisting with the saturated solution at 25 °C. However, very careful measurements by Occleshaw¹² have shown that the coexisting solid phase at the given temperature is the dihydrate $\text{NaSCN}\cdot 2\text{H}_2\text{O}$, dehydrating at 30.4 °C to anhydrous salt which, however, is prone to the formation of supersaturated metastable solutions. Dihydrate as the coexisting solid phase at 25 °C has been observed by Zhuravlev and Bychkova¹³ as well. Quite surprising, however, is that both solubilities^{11,12} of which the higher one evidently indicates the supersaturated solution, together with corresponding quite different values of γ_s and $a_{w,\text{sat}}$ calculated according to ref.⁴ led to almost identical values of $\Delta G_{\text{f}}^{\circ}(\text{NaSCN}\cdot 2\text{H}_2\text{O})$. Of course, the more reliable value of them is $\Delta G_{\text{f}}^{\circ} = -628.64 \text{ kJ mol}^{-1}$.

The mean deviation of all the results in Table II obtained in the presented manner is given on one hand by the mean deviation of standard thermodynamic data of $\Delta G_{\text{f, aq}}^{\circ}(\text{C}_c\text{A}_a)$ taken from ref.¹ (see above), and on the other hand by the mean deviation of the other used quantities, m_{sat} , γ_{sat} and $a_{w,\text{sat}}$, which, however, are not all available. Therefore, no direct deviation values of the individual considered substances can be given here. However, with respect to the fact that the experimentally attainable accuracy of the appropriate quantities can be very high in most cases, the reliability of the obtained results can be also very high.

CONCLUSIONS

a) In the most cases, the uncertainty of the published¹ standard data of $\Delta G_{\text{f, cr}}^{\circ}$ and $\Delta G_{\text{f, aq}}^{\circ}$ of selected electrolytes of the types 1-1, 1-2 and 2-1 well corresponds to the above mentioned statement;

b) in some cases, however, there are too high discrepancies between published data of individual quantities present in Eq. (1) the reason of which deserves an appropriate attention of specialists;

c) the used verification method can help to select the most probable value of the solubility from a set of highly scattered experimental data and to ascertain missing data of $\Delta G_{\text{f, cr}}^{\circ}$ or other quantities present in Eq. (1), if sufficiently reliable data of the relevant quantities are available;

d) on principle, the used verification method based on the condition of the thermodynamic equilibrium between the solid substance and its

saturated solution is commonly applicable to all types of electrolytes and, clearly, to nonelectrolytes as well.

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