VERIFICATION OF THE MUTUAL CONSISTENCY AND RELIABILITY OF THERMODYNAMIC DATA OF INORGANIC ELECTROLYTES

Jan BALEJ
Heřmanova 35, 170 00 Prague 7, Czech Republic; e-mail:balejan@seznam.cz

Received December 18, 2010
Accepted February 28, 2011

The mutual consistency and reliability of the published thermodynamic quantities $\Delta_f G°_{cr}$, $\Delta_f G°_{aq}$, solubility m_s, mean activity coefficient γ_s and water activity $a_{w,s}$ of the saturated solutions of alkali metal nitrites and selected bi-univalent compounds of Ni, Co, Zn, Cd, Pb, Cu, Mn and U at 25 °C have been checked and the obtained results discussed. The method has also been used for the calculation of lacking data $\Delta_f G°_{cr}$ of the following substances at 25 °C: $CsNO_2$, $Ni(NO_3)_2 \cdot 6H_2O$, $CoBr_2 \cdot 6H_2O$, $CoI_2 \cdot 6H_2O$, $Pb(ClO_4)_2 \cdot 3H_2O$, $Cu(NO_3)_2 \cdot 6H_2O$ and $Pb(NO_3)_2$.

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

The highest as possible accuracy and reliability of standard thermodynamic data of chemical substances $\Delta_f H°$, $\Delta_f G°$, $S°$ and $C°_p$ at the given temperature are the crucial requirements which should always be fulfilled, especially at the comprehensive thermodynamic tables (e.g. refs[1–4]). For reactions of inorganic electrolytes proceeding very often in aqueous solutions, it is very important to know standard thermodynamic data of substances not only in their pure state (e.g. refs[2–4]), but also in their standard aqueous state. From the mentioned thermodynamic tables[1–4], this requirement is only fulfilled in The NBS Tables (ref.[1]) where the uncertainty is given[5] "... in general so that the overall uncertainty lies between 8 and 80 units of the last (rightmost) digit". Nevertheless, as stated in the introduction chapters, all data in ref.[1] fulfill the requirement of the mutual consistency in the limits of their general uncertainties. Small admissible differencies can be observed e.g. by comparing values of $\Delta_f G°(C_cA_a,aq)$ given directly for $C_cA_a(aq)$ with values calculated from the sum of $\Delta_f G°$ of the appropriate ions.

In the previous paper[6], the accuracy and consistency of standard thermodynamic data[1] of some selected inorganic electrolytes of the types 1-1, 1-2 and 2-1 with the recommended thermodynamic data of m_s, γ_s and $a_{w,s}$

Collect. Czech. Chem. Commun. 2011, Vol. 76, No. 5, pp. 407–414

doi:10.1135/cccc2010153

(refs[7–10]) have been checked on the basis of the thermodynamic condition of the equilibrium between the pure solid electrolyte $C_cA_a{\cdot}nH_2O$ and its saturated aqueous solution at the given temperature expressed by the equation

$$\Delta_f G°(C_cA_a{\cdot}nH_2O,cr) = \Delta_f G°(C_cA_a,aq) + n\Delta_f G°(H_2O,l) + \\ + RT \ln (m_{C,s}{}^c m_{A,s}{}^a \gamma_s{}^{(c+a)} a_{w,s}{}^n). \qquad (1)$$

Here, $\Delta_f G°(C_cA_a{\cdot}nH_2O,cr)$, $\Delta_f G°(C_cA_a,aq)$ and $\Delta_f G°(H_2O,l)$ have their usual meaning, $m_{C,s}$ and $m_{A,s}$ represent the total cation and anion molality of the crystallizing component and γ_s and $a_{w,s}$ denote the mean activity coefficient of the crystallizing component and water activity of the saturated solution at the given temperature, and c, a and n are stoichiometric numbers. In an ideal case, when all measured quantities are absolutely correct, then the value of the quantity Φ expressed as

$$\Phi = \Delta_f G°(C_cA_a{\cdot}nH_2O,cr) - \Delta_f G°(C_cA_a,aq) - n\,\Delta_f G°(H_2O,l) \qquad (2)$$

and the value of the quantity Ψ expressed as

$$\Psi = RT \ln (m_{C,s}{}^c m_{A,s}{}^a \gamma_s{}^{(c+a)} a_{w,s}{}^n) \qquad (3)$$

must be equal, and their difference $\Delta = \Phi - \Psi = 0$. However, all data of the considered quantities have mostly been determined with some uncertainty which causes that $\Delta \neq 0$. The results of such treatment of selected electrolytes of the types 1-1, 1-2 and 2-1 have shown[6] that in the most cases, the ascertained values of Δ satisfied very well the given overall uncertainty (see above), but in some cases, quite high values of Δ have been found. The aim of the present contribution is the application of this method to check the reliability and mutual consistency of the standard thermodynamic quantities $\Delta_f G°_{cr}$ and $\Delta_f G°_{aq}$ with the known relevant data of m_s, γ_s and $a_{w,s}$ of alkali metal nitrites[11] and selected bi-univalent compounds of Fe, Ni and Co (ref.[12]), Zn and Cd (ref.[13]), Pb, Cu, Mn and U (ref.[14]) at 25 °C and to discuss eventual inconsistencies. Similarly as in the previous contribution[6], the method has also been used for the calculation of lacking values of $\Delta_f G°(C_cA_a{\cdot}nH_2O,cr)$ of some checked substances. Simultaneously, some discrepancies found in the previous contribution[6] are discussed at the end.

RESULTS AND DISCUSSION

Values of $\Delta_f G°_{cr}$ and $\Delta_f G°_{aq}$ at 25 °C of all checked substances have been taken from ref.[1], their solubilities mostly from papers bringing data of γ_s and $a_{w,s}$ (refs[11–14]). Solubility data not available there have been taken from ref.[15] In the calculations, the value[1] $\Delta_f G°(H_2O,l) = –237.129$ kJ mol^{-1} has been used. The results of the treatment are summarized in Table I. Values of the quantity Φ (equivalent to the negative value of the standard Gibbs energy of dissolution, $\Phi = -\Delta_{sol}G°(C_cA_a \cdot nH_2O,cr)$) calculated from Eq. (5) are not given in Table I. The treatment could only be performed for substances for which data of γ_s and $a_{w,s}$ have directly been given or could be determined by an admissible extrapolation from the given equations in refs[11–14]. Other substances with concentrations of the examined solutions quite lower than saturation could not be evaluated. This concerned data of $FeCl_2$, $Ni(ClO_4)_2$, $NiBr_2$, $Ni(NO_3)_2$ and $Co(ClO_4)_2$ from ref.[12], $Cd(ClO_4)_2$, $Cd(NO_3)_2$, $ZnCl_2$ and ZnI_2 from ref.[13], and $Cu(ClO_4)_2$, $CuBr_2$, $Mn(ClO_4)_2$, $MnBr_2$, UO_2Cl_2 and $UO_2(ClO_4)_2$ from ref.[14]

Before starting a discussion about the found values of Δ, it is necessary to emphasize once more the overall uncertainty of data in ref.[1] (see above). It means that the uncertainty of $\Delta_f G°$ (given in kJ mol^{-1}) of a substance with only one valid decimal digit lies between 0.8–8.0 kJ mol^{-1}, with two valid decimal digits between 0.08–0.8 kJ mol^{-1}, etc. From Table I with $\Delta_f G°$ data with one or two valid decimal digits, it can be seen that in the most cases, the obtained absolute values $|\Delta| < 0.75$ kJ mol^{-1}, i.e. they correspond very well to the overall uncertainty of standard thermodynamic data in ref.[1]. This is also valid for the pair $ZnBr_2 \cdot 2H_2O/ZnBr_2$, although in this case, an (evidently admissible) extrapolation has been used for the calculation of γ_s and $a_{w,s}$ at $m_s = 21.555$ mol kg^{-1} (ref.[15]), while values of γ and a_w have only been given for $m \le 20.100$ mol kg^{-1}. This is probably the reason why the obtained value $\Delta = 0.706$ kJ mol^{-1} is a little higher than the most in Table I. Some not too great differences in the solubility data (e.g. at $Zn(NO_3)_2$ and $PbCl_2$) did not cause any substantial difference in the values of Δ.

A quite high value $\Delta = 5.222$ kJ mol^{-1} has only been observed for the pair $CuCl_2 \cdot 2H_2O/CuCl_2$. This value, at least one order higher than at the most treated substances is not yet clear. A found printing error in the value of the 1st coefficient in the expression for $\ln \gamma = f(m)$ in ref.[14] had no influence on the given values of γ and a_w, as they all have been calculated using its correct value (0.1364012482E+1). The true reason of the high value of Δ may consist of an inaccuracy of the experimental value of Φ or Ψ, or of both values together. Assuming that the experimental value of Φ is correct, then to an ideal value $\Delta = 0$, an ideal value of the product $\gamma_s^3 a_{w,s}^2 = 0.9821$ should correspond; in reality, however, the experimentally determined and quite reliable value $\gamma_s^3 a_{w,s}^2 = 0.1195$ has been obtained. Such a great difference of this product seems to consist more probably in the lower accuracy of the values of $\Delta_f G°(CuCl_2{\cdot}2H_2O,cr)$ and/or $\Delta_f G°(CuCl_2,aq)$. This is confirmed by the fact that some discrepancy can be seen between the directly given value[1] $\Delta_f G°(CuCl_2,aq) = -197.9$ kJ mol^{-1} (with only one valid decimal digit) and the same quantity calculated as the sum of the corresponding values of the appropriate ions[1], $\Delta_f G°(Cu^{2+},aq) = 65.49$ kJ mol^{-1} and $\Delta_f G°(Cl^{1-},aq) = -131.228$ kJ mol^{-1}, leading to $\Delta_f G°(CuCl_2,aq) = -196.966$ kJ mol^{-1}. The corresponding new value $\Delta = 4.310$ kJ mol^{-1} is a little lower than the original value of 5.222 kJ mol^{-1}, but still quite high. Some inaccuracy in the solubility data seems to be unable to cause the observed high value of Δ. Any detailed elucidation of this high value of Δ deserves, therefore, an appropriate attention of specialists dealing with these substances.

TABLE I
The difference Δ for selected electrolytes of the types 1-1 and 2-1 at 25 °C[a]

Substance	$-\Delta_f G°_{cr}$ kJ mol^{-1}	$-\Delta_f G°_{aq}$ kJ mol^{-1}	m_s	γ_s	$a_{w,s}$	Ψ	Δ kJ mol^{-1}
$LiNO_2{\cdot}H_2O$	544.2	325.5	19.90	3.7389	0.30633	18.433	0.00445
$NaNO_2$	284.55	294.1	12.34	0.5654		9.63	0.081
KNO_2	306.55	315.4	34.12	0.1753		8.868	–0.018
$RbNO_2$	306.2	316.3	62.30	0.1193		10.1	0.155
$NiCl_2{\cdot}6H_2O$	1713.19	307.9	5.060	4.9067	0.5310	17.910	–0.4264
$CoCl_2{\cdot}6H_2O$	1725.2	316.7	4.3164[b]	2.5623[c]	0.6327[c]	14.501	–0.227
$Zn(ClO_4)_2{\cdot}6H_2O$	1555.2	164.1	4.300	57.3246	0.42117	31.532	0.142
$ZnBr_2{\cdot}2H_2O$	799.5	354.97	21.555[b]	8.688[d]	0.0861[d]	29.022	0.706
$Zn(NO_3)_2{\cdot}6H_2O$	1772.71	369.57	6.750	9.3013	0.37805	19.755	–0.121
			6.8165[b]	9.6029	0.37237	19.840	–0.206
$PbCl_2$	314.10	286.86	0.0390	0.4118		–27.288	0.048
			0.0392[b]	0.4115		–27.256	0.016
$CuCl_2{\cdot}2H_2O$	655.9	197.9	5.6409[b]	0.6338	0.68509	11.036	5.222
$MnCl_2{\cdot}4H_2O$	1423.6	490.8	6.155[b]	1.9393	0.5577	16.087	–0.371
$UO_2(NO_3)_2{\cdot}6H_2O$	2585.3	1176.0	3.323[b]	2.175	0.7259	13.381	0.093

[a] Solubility data without index from papers bringing data of γ_s and $a_{w,s}$; [b] ref.[15]; [c] admissible extrapolation after ref.[12]; [d] admissible extrapolation after ref.[13]

Similarly as in the previous paper[6], the data of γ_s and $a_{w,s}$ given in refs[11–14] have been used for the calculation of lacking data of $\Delta_f G°(C_cA_a \cdot nH_2O,cr)$ of substances coexisting with their saturated solutions at 25 °C when all other data in Eq. (*1*) are known with a sufficient reliability. The lacking value has been calculated using the expression

$$\Delta_f G°(C_cA_a \cdot nH_2O,cr) = \Delta_f G°(C_cA_a,aq) + n\Delta_f G°(H_2O,l) + \Psi. \qquad (4)$$

This concerned the following solid substances: $CsNO_2$, $Ni(NO_3)_2 \cdot 6H_2O$, $CoBr_2 \cdot 6H_2O$, $CoI_2 \cdot H_2O$, $Pb(ClO_4)_2 \cdot 3H_2O$, $Cu(NO_3)_2 \cdot 6H_2O$ and $Pb(NO_3)_2$. The value of $\Delta_f G°(Pb(ClO_4)_2,aq)$, not given in ref.[1], has been calculated from the appropriate values of individual ions[1]. The solubilites of the considered substances not given directly in refs[11–14] have been taken from ref.[11]. For the pair $Cu(NO_3)_2 \cdot 6H_2O/Cu(NO_3)_2$, an admissible extrapolation in the calculation of γ_s and $a_{w,s}$ after ref.[14] has been used, because the solubility m_s = 8.0132 mol kg^{-1} (ref.[15]) is only a little higher than the maximum measured[14] molality m = 7.840 mol kg^{-1}. All results are summarized in Table II.

As can be seen, the differences in values of $\Delta_f G°(C_cA_a \cdot nH_2O,cr)$ caused by some differences in solubility data lie in the range of the common overall uncertainty of data in ref.[1] (see above). Therefore, it can be concluded that the so obtained data of the considered substances at 25 °C in Table II can be taken as sufficiently reliable and consistent with the other relevant thermodynamic data of these substances.

In addition, some elucidation can be made to the previously observed high values of Δ at some substances[5], the reason of which has not been discussed there. At first, this concerns the high value Δ = –3.456 kJ mol^{-1} at $NaNO_3$. According to a careful evaluation of thermodynamic properties of the $NaNO_3 + H_2O$ system by Archer[16], the following value γ_s = 0.31824 at 25 °C could be derived for m_s = 10.839 mol kg^{-1} (ref.[16]), which is quite different from the previously used value γ_s = 0.641 at m_s = 10.830 mol kg^{-1} according to ref.[7] Using these values, the following value Ψ = 6.1389 kJ mol^{-1} has been obtained, leading, with the same value[6] Φ = 6.15 kJ mol^{-1}, to the final value Δ = 0.0111 kJ mol^{-1}. This very low value of Δ excellently testifies the high accuracy of the original standard thermodynamic data[1] of this substance and their full consistency with other relevant thermodynamic data given in ref.[16], namely m_s and γ_s.

Another comment can be done to a high value Δ = –6.725 kJ mol^{-1} observed[6] for the pair $SrCl_2 \cdot 6H_2O/SrCl_2$. The reason of this finding could consist either of an erroneous value of Ψ, or erroneous value of Φ, or both erroneous values together. Assuming Δ = 0, then to an assumed correct value Φ = 3.764 kJ mol^{-1}, an ideal value of the product $\gamma_s a_{w,s}{}^2$ = 0.297 should correspond. In reality, a distinctly different value $\gamma_s a_{w,s}{}^2$ = 0.7338 has been obtained, which testifies that the assumption about a correct value of Φ cannot be valid. This deduction seems to be supported on comparing the value Φ = 3.764 kJ mol^{-1} with the same quantity of other hydrated halides of alkaline earths[1] which all lie in the range between 16.6 (for $SrBr_2 \cdot 6H_2O$,cr) and 31.46 kJ mol^{-1} (for $CaBr_2 \cdot 6H_2O$,cr). Accordingly, the value Φ($SrCl_2 \cdot 6H_2O$,cr) = 3.764 kJ mol^{-1} seems to be too low. In recent thermodynamic tables[17], a quite different value $\Delta_f G°$($SrCl_2$,aq) = –826.321 kJ mol^{-1} (based on the the value $\Delta_f G°$(Sr^{2+},aq) = –563.83 ± 0.8 kJ mol^{-1} after ref.[18]) is given, in comparison to the original value in ref.[1] (–821.91 kJ mol^{-1}). This leads to Φ = 8.175 kJ mol^{-1} and to a distinctly lower value Δ = –2.314 kJ mol^{-1}, in comparison with the original value (see above). Nevertheless, also this new value of Δ is too high and deserves further explication.

Further comment can further be done to a quite high value Δ = –6.381 kJ mol^{-1} ascertained previously[6] for $K_2Cr_2O_7$. This value of Δ corresponds though to the announced limits of the uncertainty of the standard thermodynamic data[1] (see above) because all their values of $\Delta_f G°$ have been given with only one valid decimal digit[1], but with respect to the quite reliable

TABLE II

Values of $\Delta_f G°(C_c A_a \cdot n H_2O$,cr) at 25 °C calculated according to Eq. (*4*)[a]

Substance	$-\Delta_f G°_{aq}$ kJ mol^{-1}	m_s	γ_s	$a_{w,s}$	Ψ	$-\Delta_f G°_{cr}$ kJ mol^{-1}
$CsNO_2$	324.2	36.00	0.2265		10.404	313.8
$CoBr_2 \cdot 6H_2O$	262.3	5.445	18.2746	0.42162	24.802	1660.27
		5.304[b]	16.804	0.43532	24.459	1660.61
$CoI_2 \cdot H_2O$	157.7	6.500	116.5874	0.28334	33.989	360.84
		6.650[b]	121.163	0.27725	34.121	360.71
$Co(NO_3)_2 \cdot 6H_2O$	276.9	5.620	4.5495	0.48755	16.857	1682.82
		5.664[b]	4.6472	0.48325	16.941	1682.73
$Pb(ClO_4)_2 \cdot 3H_2O$	41.47	10.830	44.0089	0.14676	35.027	717.83
$Pb(NO_3)_2$	246.93	1.830	0.0938		–9.669	256.60
		1.811[b]	0.0942		–9.716	256.65
$Cu(NO_3)_2 \cdot 6H_2O$	157.02	8.0132[b]	5.9165[c]	0.3489[c]	16.473	1563.32

[a] Solubility data without index from papers containing data of γ_s and $a_{w,s}$; [b] ref.[15]; [c] admissible extrapolation after ref.[14]

data of m_s and γ_s of this substance, it can be expected that more precise values of $\Delta_f G°_{cr}$ and/or $\Delta_f G°_{aq}$ of the mentioned substance could be obtained by new determination of the appropriate thermochemical data.

At the end, it can be concluded that the presented results have confirmed the sufficient reliability and consistency of the published standard thermodynamic data of $\Delta_f G°_{cr}$ and $\Delta_f G°_{aq}$ of some compounds of Ni, Co, Zn, Cd, Pb, Cu, Mn and U at 25 °C with their data of m_s, γ_s and $a_{w,s}$. On the other hand, a too high value of the quantity Δ testified some discrepancies and inconsistencies in the so far published thermodynamic data for the pair $CuCl_2 \cdot 2H_2O/CuCl_2$. The same method has also been used for the determination of lacking data of $\Delta_f G°(C_cA_a \cdot nH_2O,cr)$ at 25 °C of the following substances: $CsNO_2$, $Ni(NO_3)_2 \cdot 6H_2O$, $CoBr_2 \cdot 6H_2O$, $CoI_2 \cdot H_2O$, $Pb(ClO_4)_2 \cdot 3H_2O$, $Cu(NO_3)_2 \cdot 6H_2O$ and $Pb(NO_3)_2$. Some explication could also be given to the previously found[6] high values of Δ of some checked substances. The results confirmed the overall usefulness of this method applicable commonly to all types of electrolytes and non-electrolytes as well. At the end, it must still be emphasized the necessity to experimentally determine values of γ and a_w in the full concentration range, i.e. up to the saturated or, if possible, to the supersaturated state. It is further desirable that the solubility data should be determined with the highest as possible accuracy as well, as the so far published data often exhibit quite great scatter and do not correspond to their importance in the evaluation of accurate as possible standard thermodynamic data of chemical substances.

REFERENCES

1. Wagman D. D., Evans W. N., Parker V. B., Schumm R. H., Halow I., Bailey S. M., Churney K. L., Nuttall R.: *J. Phys. Chem. Ref. Data* **1982**, *11*, Suppl. 2.
2. Chase M. W., Jr., Davies C. A., Downey J. R., Jr., Frurip D. J., McDonald R. A., Syverud A. N.: *J. Phys. Chem. Ref. Data* **1985**, *14*, Suppl. 1.
3. Barin I.: *Thermochemical Data of Pure Substances.* VCH, Weinheim 1989.
4. Knacke O., Kubaschewski O., Hesselmann K.: *Thermochemical Properties of Inorganic Substances*, 2nd ed., Vol. I and II. Springer, Berlin 1991.
5. Ref.[1], pp. 2–16.
6. Balej J.: *Collect. Czech. Chem. Commun.* **2010**, *75*, 21.
7. Hamer W. J., Wu Y.-Ch.: *J. Phys. Chem. Ref. Data* **1972**, *1*, 1047.
8. Goldberg R. N.: *J. Phys. Chem. Ref. Data* **1981**, *10*, 671.
9. Wishaw B. F., Stokes R. H.: *Trans. Faraday Soc.* **1954**, *50*, 952.
10. Goldberg R. N., Nuttall R. L.: *J. Phys. Chem. Ref. Data* **1978**, *7*, 263.
11. Staples B. R.: *J. Phys. Chem. Ref. Data* **1981**, *10*, 765.
12. Goldberg R. N., Nuttall R. L., Staples B. R.: *J. Phys. Chem. Ref. Data* **1979**, *8*, 923.
13. Goldberg R. N.: *J. Phys. Chem. Ref. Data* **1981**, *10*, 1.
14. Goldberg R. N.: *J. Phys. Chem. Ref. Data* **1979**, *8*, 1005.

15. Broul M., Nývlt J., Söhnel O.: *Solubility in Inorganic Two-Component Systems*. Academia, Prague 1981.
16. Archer D. G.: *J. Phys. Chem. Ref. Data* **2000**, *29*, 1141.
17. Phillips S. L., Hale F. V., Silvester L. F.: *Thermodynamic Tables for Nuclear Waste Isolation,* Vol. 1: *Aqueous Solution Database*, p. 157. Lawrence Berkeley National Laboratory, Lawrence Berkeley National Laboratory 2008.
18. Busenberg E., Plummer L. N., Parker V. B.: *Geochim. Cosmochim. Acta* **1984**, *48*, 2021.