

Letter

## Comments on the Remarks of V. P. Vasil'ev on Plyasunov and Grenthe: Extrapolation of Enthalpies of Reaction in Electrolyte Systems to Infinite Dilution<sup>1</sup>

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Vasil'ev<sup>2</sup> claims that 'incorrect use of concepts and definitions, generally accepted in thermochemistry of solutions has led the authors to certain erroneous conclusions'. Let us explore the basis for this statement. Our paper describes the use of semi-empirical methods for the extrapolation of standard enthalpies of reaction [eqn. (1) in Ref. 1] in ionic media to standard enthalpies of reaction in the pure water solvent. The main text, pp. 571–577, compares the Pitzer and the Brønsted–Guggenheim–Scatchard models with the 'empirical approach of Wang *et al.* (Refs. 3 and 4 in Ref. 1).' As Vasil'ev made no comments on this part of our work we assume that it does not contain any 'incorrect use of concepts and definitions... (and therefore no) erroneous conclusions'. Vasil'ev remarks seems to refer the final section in our paper entitled 'Use of the Vasil'ev–Yasinskii equation'. Vasil'ev has two main critical comments. In the first he claims that eqns. (2) and (16) in Ref. 1 are equivalent:

$$\Delta_r H - \Delta_r H^\circ = \sum_i p_i L_{2,i} + r L_1 \quad [\text{eqn. (2) in Ref. 1}]$$

$$\Delta_r H - \Delta_r H^\circ = \sum_i p_i L_{\phi,i} \quad [\text{eqn. (16) in Ref. 1}]$$

where  $p$  and  $r$  are stoichiometric coefficients in the equation

$$\sum_i p_i Q_i + r H_2O(1) = 0 \quad [\text{eqn. (1) in Ref. 1}]$$

$L_{2,i}$  and  $L_1$  are the relative partial molar enthalpy of reactants/products and water, respectively, while  $L_{\phi,i}$  is the relative apparent molar enthalpy of the reactants/products.

To demonstrate the equivalence between eqns. (2) and (16) Vasil'ev used the well known relation for the enthalpy of dilution of a binary salt–water system [eqn. (a) in Ref. 2]:

$$n_2 \Delta_\phi = -n_1 L_1 - n_2 L_2 = -n_2 L_\phi \quad [\text{eqn. (a) in Ref. 2}]$$

and equated eqns. (2) and (16) to obtain

$$\sum_i p_i L_{2,i} + r L_1 = \sum_i p_i L_{\phi,i} \quad [\text{eqn. (b) in Ref. 2}]$$

However, in eqns. (a) and (b) the coefficients denote completely different quantities ( $n_1$  and  $n_2$  are the number of moles of water and solute, respectively, in the binary mixture, while  $r$  and  $\sum_i p_i$  are the stoichiometric coefficients of a reaction). For example, for a reaction in an ionic medium where water does not participate in the reaction,  $r=0$ .

Vasil'ev's second objection is that his eqn. (c)<sup>2</sup>

$$H_{2,i} = H_{2,i}^\circ + \phi_{2,i}$$

(which for consistency should be written  $H_{2,i} = H_{2,i}^\circ + L_{\phi 2,i}$ ), never appeared in the Vasil'ev–Yasinskii paper,<sup>3</sup> and that  $\phi_i$  in Ref. 3 stands for the enthalpy of the solution as a whole. In the original paper by Vasil'ev and Yasinskii (Ref. 3, p. 322 in the English translation) there is a discussion using the following scheme for the complex formation reaction



where 'we will have a strict thermodynamic equation:

$$\begin{aligned}\Delta H_T = & \Delta H_T + \phi_L(\text{ML}_n, \text{soln.}; n\text{H}_2\text{O}) \\ & + \phi_L(\text{K}_n\text{L}, \text{soln.}; n\text{H}_2\text{O}) \\ & - \phi_L(\text{MA}, \text{soln.}; n\text{H}_2\text{O}) \\ & - n\phi_L(\text{KL}, \text{soln.}; n\text{H}_2\text{O})' \quad [\text{eqn. (7) in Ref. 3}]\end{aligned}$$

Here  $\Delta H_T$ ,  $\Delta H_T^\circ$  and  $\phi_L$ , stand for the enthalpy change for the reaction in solution of finite concentration, at infinite dilution, and for the relative apparent molar enthalpy, respectively. We consider eqn. (c) to be a consequence of eqn. (7).

## References

1. Plyasunov, A. V. and Grenthe, I. *Acta Chem. Scand.* 50 (1996) 571.
2. Vasil'ev, V. P. *Acta Chem. Scand.* 51 (1997) 813.
3. Vasil'ev, V. P. and Yasinskii, F. N. *Zh. Neorg. Khim.* 23 (1978) 579 (*In Russian*). *Russ. J. Inorg. Chem.* 23, *Engl. Transl.* (1978) 321.

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