

Letter to the Editor

Fundamental Definition of Solution Thermochemistry and Extrapolation of Enthalpies of Reaction to Infinite Dilution. Comments on a Paper by A. V. Plyasunov and I. Grenthe

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Vasil'ev, V. P., 1997. Fundamental Definition of Solution Thermochemistry and Extrapolation of Enthalpies of Reaction to Infinite Dilution. Comments on a Paper by A. V. Plyasunov and I. Grenthe. – Acta Chem. Scand. 51: 813–814. © Acta Chemica Scandinavica 1997.

The significance of the problem of the calculation of standard enthalpies of reaction in solution is evident, and in this connection the paper by Plyasunov and Grenthe¹ attracts attention. Unfortunately, incorrect use of concepts and definitions, generally accepted in thermochemistry of solutions,² has led the authors¹ to certain erroneous conclusions.

Some misunderstandings begin with a comparison of eqns. (2) and (16)

$$\Delta_r H = \Delta_r H_m^\circ + \sum p_i L_{2i} + r L_1 \quad (2)$$

$$\Delta_r H_m(I) = \Delta_r H_m^\circ + \sum p_i L_{\phi,i}(I) \quad (16)$$

The authors¹ point out that 'eqn. (16) was postulated; no attempts to deduce this formula from more general thermodynamic relations have been undertaken' and then conclude 'It is obvious that eqns. (2) and (16) are not consistent with one another'.

Let us consider whether this is really the case. From the definition of L_ϕ in Ref. 1 and in Ref. 2 as enthalpy of dilution of an electrolyte to infinite dilutions with opposite sign, it follows that

$$n_2 \Delta_\phi = -n_1 L_1 - n_2 L_2 = -n_2 L_\phi \quad (a)$$

where ΔH_D is the enthalpy of dilution to infinite dilution, L_1 and L_2 are the relative partial molar enthalpies of water and solute, respectively, and L_ϕ is the apparent relative molar enthalpy of the solution. The same formula (a) is obtained, as one can see, when comparing eqns. (2) and (16):

$$\sum p_i L_{2i} + r L_1 = \sum p_i L_{\phi,i} \quad (b)$$

Thus, eqns. (2) and (16) are completely consistent with one another. The difference is only in that non-ideality of electrolyte solutions in eqn. (2) is taken into

account as the relative partial molar enthalpy of the components of the solution, but in eqn. (16) it is taken into account as the apparent relative molar enthalpy of the solution as a whole. Formula (b) shows that this is the same thing, and makes it clear why 'no attempts to deduce this formula from more general thermodynamic relations have been undertaken'. We consider that deduction is unnecessary if formula (a) is available.²

The reason for the 'discrepancy' between eqns. (2) and (16) is seen by the authors¹ in the wrong assumption that

$$H_{2,i} = H_{2,i}^\circ + \varphi_{2,i} \quad (c)$$

asserting¹ that eqn. (c) is presented in our paper.³

Equation (c) is wrong, but in our paper³ there is nothing of the kind. According to index 2, formula (c) contains the enthalpy of the solute, but in our paper³ φ_i has no index 2, and according to the generally accepted designation² presents the enthalpy of the solution, but not enthalpy of only one of its components. Thus the erroneous appreciation in Ref. 1 of the V–Y equation is the consequence of a misunderstanding. The V–Y equation is based on strict thermodynamic definitions and needs no correction.

The value of $\Delta_r H(I)$ in eqn. (16) is not merely the enthalpy of mixing of the reacting substances, but the enthalpy change as the result of reaction at constant total ionic strength I with enthalpy of dilution of the reaction participant at this ionic strength and completeness of the reaction under the given concentration conditions taken into account.^{3,4}

The validity of eqns. (15) and (16) is shown by the results of the calorimetric investigations of a large

number of reactions, carried out in the presence of various supporting electrolytes.⁴ The $\Delta_r H^\circ$ value obtained at extrapolation according to eqn. (15) remains the same independent of the nature of the supporting electrolyte (NaClO_4 , NaNO_3 , KNO_3 , etc.), this impartially affirming the reliability of the data obtained according to eqn. (15).

In the system, in which it was not necessary to take into account the completeness of reaction and one could compare the results obtained according to eqn. (15) and the results obtained directly on enthalpy of dilution of the participants of the reaction, the values $\Delta_r H^\circ$ coincide quite satisfactorily. The data in Refs. 1 and 4 for the enthalpy of dissociation of water may be used as an example of this.

References

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Received December 2, 1996.