Enthalpies of Transfer involving Ionic Transition States: the Redundance of Extrathermodynamic Assumptions

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It is pointed out that the calculation of transition state enthalpies of transfer for reactions involving ions does not necessitate the estimation of thermodynamic quantities for single ions. The procedure is illustrated by data on the reaction between ethyl acetate and sodium hydroxide in water–dimethyl sulphoxide mixtures.

HYDROXIDE ion-catalysed reactions have been observed to be greatly accelerated—with attendant changes of the energy and entropy of activation—as the reaction medium is varied from water to dimethyl sulphoxide–water mixtures. The measured enthalpies of solution of the reactants in water and in mixed solvent ($\Delta H_w, \Delta H_m$) can be combined with observed enthalpies of activation ($\Delta H^\ddagger{}_w, \Delta H^\ddagger{}_m$) to give enthalpies of transfer for the transition state from water to mixed solvents ($\Delta H^\ddagger{}_{transfer}$). The analysis of activation parameters in such terms is of interest because it throws light on the differential solvent effect on reactants and transition states.[1]

For a bimolecular reaction, ΔH_w and ΔH_m are each the sum of two separately determined enthalpies of solution for the two reactant species. When one of the reactants is the hydroxide ion, this thermochemical sum has, by some workers, been tackled as follows.[2,3] The experimentally determined enthalpy of solution of sodium hydroxide (which is itself a sum of contributions from the two ions) is used to evaluate the enthalpy of solution of the hydroxide ion (a thermodynamic property relating to a single ion) by the application of an extra-thermodynamic assumption, such as the one that the enthalpies of transfer of tetraphenylphosphonium and tetraphenylborate ions are equal,[3,4] or that the transfer enthalpies of tetra-n-butylammonium and tetra-n-butylborate are the same.[2] (For the history of the assumptions see references 3 and 4.)

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[1] For a review see M. H. Abraham, *Progr. Phys. Org. Chem.*, 1974, **12**, 1.

[2] P. Haberfield, J. Friedman, and M. F. Pinkston, *J. Amer. Chem. Soc.*, 1972, **94**, 71.

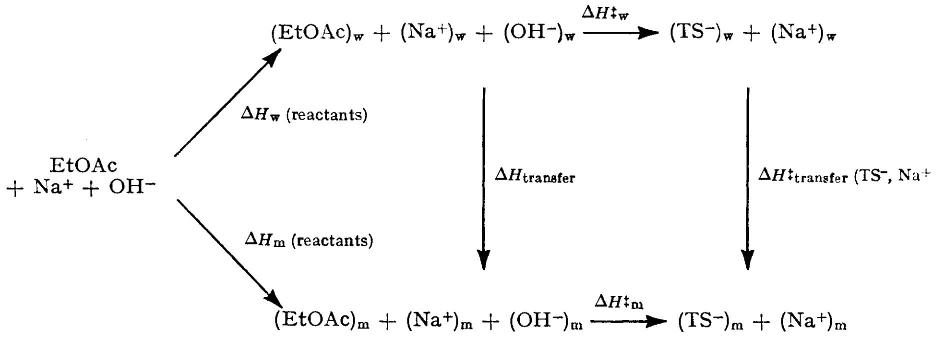
[3] R. Fuchs, C. P. Hagan, and R. F. Rodewald, *J. Phys. Chem.*, 1974, **78**, 1509.

[4] R. Fuchs and C. P. Hagan, *J. Phys. Chem.*, 1973, **77**, 1797.

It is not the object of the present paper to assess the relative merits of these assumptions or to disentangle the conflicting conclusions about enthalpies of transfer that have resulted from their applications. Instead, we wish to point out that this application of extrathermodynamic assumptions is altogether unnecessary. The problem under consideration involves only electrically neutral combinations of ions, and only *sums* of enthalpies in such combinations are required for its elucidation. Such sums are thermodynamically defined.[5]

The principle is well understood and commonly applied in the discussion of chemical equilibria.[6] It is also implicitly recognised in some treatments involving ionic transition states.[7] However, some recent discussions have quite unnecessarily been couched in terms of single-ion parameters. The need for a brief explicit statement of the basic principle as applied to transition states is therefore indicated.

The illustrated Scheme represents the hydroxide ion-catalysed hydrolysis of ethyl acetate which has been the subject of recent studies.[2,3] The subscripts denote solution in water (w) and in the mixed solvent (m), respectively. The symbol TS^- refers only to the anion part of the transition state, which is accompanied by its counter-ion Na^+.



SCHEME

Summary of transfer enthalpies (kcal mol^{-1}) relating to the reaction of ethyl acetate with sodium hydroxide in dimethyl sulphoxide–water mixtures (data from Fuchs *et al.*[3])

Mole% Me_2SO	$(\Delta H^‡_m - \Delta H^‡_w)$ [a]	$\Delta H_{transfer}$ (Na^+, OH^-)	$\Delta H_{transfer}$ (EtOAc)	$\Delta H_{transfer}$ (reactants)	$\Delta H^‡_{transfer}$ (TS^-, Na^+)	$\Delta\Delta H^t$ [b]	$\delta\Delta H_{transfer}$ [c]
0	(0)	(0)	(0)	(0)	(0)	(0)	(0)
3	−0.2	0	0.9	0.9	0.7	0.4	0.7
6	−0.4	0	1.7	1.7	1.3	0.5	1.3
15	−0.2	0.8 [d]	3.3	4.1	3.9	4.1	3.1
28	0.3	4.3 [d]	4.2	8.5	8.8	10.5	4.5
51	0.9	7.1 [d]	3.8	10.9	11.8	16.9	4.7
58	1.1	7.5 [d]	3.6	11.1	12.2	18.1	4.7

[a] Measurements by Tommila and Murto.[8] [b] Calculated by Fuchs *et al.*[3] *via* single-ion enthalpies. [c] Defined in equation (ii) [d] Values interpolated from data given by Fuchs and Hagan.[4]

From the cycles in the Scheme, we obtain equation (i),

$$\Delta H^‡_{transfer}\,(TS^-,Na^+) = \Delta H_{transfer}\,(EtOAc) + \Delta H_{transfer}\,(Na^+,OH^-) + \Delta H^‡_m - \Delta H^‡_w \quad (i)$$

which allows us to compare $\Delta H^‡_{transfer}$ (TS^-,Na^+) with $\Delta H_{transfer}$ (Na^+,OH^-). In the absence of strong and specific inter-ionic effects, which may be deemed to be absent if the data are extrapolated to infinite dilution, equation (ii) will apply. Equations (i) and (ii) allow us

$$\begin{aligned}\delta\Delta H_{transfer} &= \Delta H^‡_{transfer}\,(TS^-,Na^+) - \Delta H_{transfer}\,(Na^+,OH^-)\\ &= \Delta H^‡_{transfer}\,(TS^-) - \Delta H_{transfer}(OH)^- \quad (ii)\end{aligned}$$

to determine the differential solvent effect on the transition state ion TS^- and the hydroxide ion, which we regard as the only unambiguously attainable objective of this type of treatment. The Table summarises the primary and derived thermochemical quantities, using the experimental data given or cited by Fuchs *et al.*[3] For the sake of comparison the penultimate column of the Table gives the values of '$\Delta\Delta H^t$' or '$\Delta\Delta H_s$ (transition state)' (the enthalpy of transfer of TS^- calculated by Fuchs *et al. via* single-ion enthalpies). If one accepts the procedure used for calculating the single-ion enthalpy of solution of the hydroxide ion,[3] the discrepancy between this value and $\Delta H^‡_{transfer}$ (TS^-, Na^+) corresponds to the enthalpy of transfer of the sodium ion. Alternatively, the discrepancy may be thought to point to the pitfalls inherent in the use of extrathermodynamic assumptions in problems where they are avoidable.

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[5] See, *e.g.*, L. Benjamin and V. Gold, *Trans. Faraday Soc.*, 1954, **50**, 797.

[6] See, *e.g.*, J. W. Larsen, K. Amin, S. Ewing, and L. L. Magid, *J. Org. Chem.*, 1972, **37**, 3857.

[7] E. M. Arnett and D. R. McKelvey, *Rec. Chem. Progr.*, 1965, **26**, 185; P. T. McTigue and A. R. Watkins, *Austral. J. Chem.*, 1972, **25**, 777.

[8] E. Tommila and M. L. Murto, *Acta Chem. Scand.*, 1966, **20**, 923.