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Thermodynamic Functions of Transfer of Single Ions from Water to Nonaqueous and Mixed Solvents

PART 4: SELECTION OF EXTRATHERMODYNAMIC ASSUMPTIONS

Prepared for publication by

Y. MARCUS

Department of Inorganic and Analytical Chemistry,
The Hebrew University of Jerusalem, Israel

Thermodynamic functions of transfer of single ions from water to nonaqueous and mixed solvents: Part 4 – The selection of extrathermodynamic assumptions

Abstract - The selection of an extrathermodynamic assumption for the
division of standard thermodynamic functions of transfer of electrolytes
from a reference solvent to other solvents is discussed. Reasons for
choosing water as the reference solvent are given. Advantages and draw-
backs of approaches concerning the Gibbs energy of transfer: real poten-
tials, negligible liquid junction potential, electrostatic models,
extrapolation methods, reference ion, reference ion/molecule redox couple,
and reference electrolyte, are discussed. The least objectionable is
the last one, with tetraphenylarsonium (or -phosphonium) tetraphenylborate
as the reference electrolyte. This has the additional advantage that it
can be applied also to enthalpy and entropy of transfer data.

CONTENTS

4.1 INTRODUCTION

The thermodynamics of the transfer of an electrolyte from one solvent (S_1) to another (S_2)
can be studied experimentally by a variety of methods: electrometrically, calorimetrically,
by solubility measurements, etc. A large body of information has been collected over the
years on the standard molar Gibbs free energy of transfer, ΔG_t^∞ (solute, $S_1 \rightarrow S_2$), the stand-
ard molar enthalpy of transfer, ΔH_t^∞ (solute, $S_1 \rightarrow S_2$) and the derived standard molar entropy
of transfer, ΔS_t^∞ (solute, $S_1 \rightarrow S_2$). Standard molar volumes of transfer ΔV_t^∞ (solute, $S_1 \rightarrow S_2$)
have been reported less extensively, and even less than that standard molar heat capacities
of transfer, ΔC_{pt}^∞ (solute, $S_1 \rightarrow S_2$). The superscript ∞ denotes here the hypothetical ideal
1 mol/dm³ solution of the electrolyte solute in the two solvents S_1 and S_2, so that ion-ion
interactions are excluded. On the other hand, these standard molar thermodynamic quantities
have a strong bearing on the ion-solvent interactions , and relate directly to the solvation
of the ions in the two solvents.

The interpretation of these thermodynamic quantities in terms of individual ionic solvation,
with the use of appropriate interaction models, can form the basis for their systematization.
It can also form the basis for their prediction from suitable properties of the ions and the
solvents for systems so far not measured. For this purpose it is necessary to know the
contributions of the individual ions to the thermodynamic quantities measurable for complete
electrolyte solutes only. The estimation of these individual ionic contributions must, how-
ever, be based on extrathermodynamic assumptions.

Extrathermodynamic assumptions for the splitting of thermodynamic quantities of solvation and of transfer have been proposed by many authors and examined critically by some. Conway[1] has summarized the merits of, and difficulties with, these assumptions with regard to the hydration of ions (i.e., their solvation by water), and has made some recommendations. Parker and Alexander[2] have examined some of the proposed methods regarding ΔG_t^∞ (ion, $S_1 \to S_2$), and more comprehensive comparisons and evaluations have been made by Popovych[3,4] and Marcus[5], among others.

In recent publications the present author presented a compilation of data on ΔG_t^∞ (ions, W→S)[6] and $\underline{H}_t$ (ions, W → S), where W denotes water and S a nonaqueous solvent. He also evaluated these data on the basis of preferred extrathermodynamic assumptions, and arrived at a set of selected data that he recommended. This paper provides a renewed examination of the various extrathermodynamic assumptions that have been proposed, not only concerning $\underline{G}_t$ (ion, W → S) but also the other thermodynamic functions, including the standard enthalpy and entropy of transfer.

4.2 CHOICE OF THE REFERENCE SOLVENT

Thermodynamic quantities of transfer deal with the transfer of the solute (ion) from a reference solvent S_1 to all other solvents, symbolized here by S_2, which include both pure solvents and mixtures. Although the compilations referred to above[6,7] identified S_1 = W = water (and S_2 = S, a pure nonaqueous solvent), this identification needs justification.

There are several aspects to the choice of the reference solvent: the feasibility of the use of S_1 in the experimental setup envisaged, its inertness towards the electrolyte beyond solvation (avoidance of extensive solvolysis), experimental convenience, and the ready availability of S_1 in pure form (uncontaminated by more reactive or better solvating solvents) are some. Another important aspect is the extensiveness of the knowledge of the interactions that S_1 undergoes with ions. From several of these points of view some polar aprotic solvent, such as acetonitrile, may be preferred. These include the better reproducibility of liquid junctions and the better stability of the measured e.m.f.'s in certain cells than if water is employed. In the case of solubility measurements of a reference electrolyte, such as tetraphenylarsonium tetraphenylborate, an argument in favor of the use of a polar aprotic solvent for the reference solvent S_1 was the relative instability of the anion in water.

Another argument was the extremely low solubility of this electrolyte in water, that is difficult to measure. A further argument in favor of the choice of acetonitrile (relative permittivity, ε = 37.5 at 25 °C) or methanol (ε = 32.7 at 25 °C) is that many of the transfers of interest are to solvents having relative permittivities in the range of 30 to 45 (to quote a few: ethylene glycol, ε = 37.9; nitromethane, ε = 35.8; nitrobenzene, ε = 34.8; N,N-dimethylformamide, ε = 36.7; N,N-dimethylacetamide, ε = 37.8; dimethyl sulfoxide, ε = 46.7; N-methyl-pyrrolidinone, ε = 32.0; hexamethylphosphoric triamide, ε = 30.0). Errors due to inadequate consideration of salt-effect activity coefficient corrections to obtain standard quantities of transfer are minimized if the relative permittivities of S_1 and S_2 are similar.

Notwithstanding these arguments, however, there are also ones in favor of the choice of water as the reference solvent S_1. Some of the above-mentioned methodological objections to water can be overcome with more advanced experimental methodology. It is certainly true that water is more readily purified from other solvating impurities than are most solvents from water. Furthermore, there has been no universal agreement as to which polar aprotic solvent to choose on the ground of experimental convenience, acetonitrile and methanol being favorites, but by no means generally endorsed choices.

The better criterion for the choice is, therefore, the availability of extensive knowledge of the solvation characteristics of ions in the solvent S_1, together with theoretical insight into the interactions involved. From this standpoint water is unique as the reference solvent S_1, in view of the thorough knowledge of hydration that already exists [58,59] and that is constantly being augmented[60,61]. This holds true, notwithstanding the imperfect understanding at present of some features of ion hydration, such as the role of the structure of the water.

Furthermore, the standard molar Gibbs energies of transfer of individual ions from water as the reference solvent to many nonaqueous solvents have been used[62] to fix the standard potentials of electrodes in these solvents relative to the standard hydrogen electrode in water. The extensiveness of the standard electrode potentials known in water[63] is a great asset in this connection. Likewise, the temperature coefficients for the standard potentials in nonaqueous solvents have been obtained[62] from the standard entropies of transfer of the ions into them from the reference solvent water.

A large body of data exists concerning the standard thermodynamic functions of transfer of electrolytes from the reference solvent water to aqueous-organic solvent mixtures, considerably more than on the transfer between nonaqueous solvents and their mixtures. These data have not yet been systematically analyzed in terms of the contributions of the individual ions, this being a goal of the continuation of this series of reports from IUPAC Commission V.5. One aspect of this transfer, however, has already been touched on by the Commission, namely the criteria for standardization of pH measurements in organic solvents and water + organic solvent mixtures of moderate to high permittivities[64]. Here, again, water is employed as the reference solvent, where the standardization of the pH scale is already well established.

Henceforth, therefore, the reference solvent that has been selected is water, and the symbol W will represent it, exclusively.

4.3 ASSUMPTIONS CONCERNING THE GIBBS ENERGY OF TRANSFER

The decision concerning the choice of the reference solvent is arbitrary, but not so is the decision regarding the division of ΔG_t^∞ of an electrolyte into the ionic contributions, if these are to throw some light on the interactions involved. Ion-ion interactions make no contribution at all to the standard Gibbs free energy of transfer. Therefore ΔG_t^∞ (electrolyte , W → S) is additive with respect to the ionic contributions, weighted according to their stoichiometric coefficients. This is an important criterion by which any absolute scale for ΔG_t^∞ (i, W → S), where i is a single ion, must be judged. Scales of ΔG_t^∞ (i, W → S) have been proposed that provide values for ions of one kind of charge only. For example, polarographic half-wave potentials versus a certain reference electrode have been converted to ΔG_t^∞ (i, W → S) values of metallic cations[9]. No corresponding values for anions can be obtained by this method, however. Such scales are less useful than those based on data for complete electrolytes, since they cannot be checked by means of the criterion of additivity (they can, if it is demonstrated that the values are independent of the nature of the anions present).

Several schemes have been proposed for effecting the division of standard molar Gibbs energies of transfer of electrolytes into their ionic contributions. They may be classified into the following categories:

   a) The determination of "real" potentials;
   b) The assumption of a negligible liquid junction potential;
   c) Electrostatic models;
   d) Extrapolation methods;
   e) The assumption of a constant Gibbs energy of solvation of a reference ion;
   f) The assumption that a reference ion and its uncharged analog have the same difference in ΔG^∞ to all solvents;
   g) The assumption that a reference pair of ions of opposite sign have the same ΔG_t^∞ to all solvents.

Following is a discussion of the merits and drawbacks of these extrathermodynamic assumptions and a more detailed reasoning behind the choice of the method finally selected.

(a) Real potentials[9-12] are obtained from the measurement of the compensating voltage in a cell where the two half-cells are separated by a gas gap. In a cell like this, one of the solutions flows down along the walls of a vertical glass tube, the other flows as a jet down the axis of the tube, while a gas (air or nitrogen) flows between the solutions. The gas carries along with it vapors that might otherwise condense into the wrong solvent.

For obtaining the real potential of Ag^+ ions the cell A may serve:

   $Ag/AgNO_3$ in $W/gas/AgNO_3$ in S/Ag (A)

and for Cl^- ions the cell B:

   $Ag/AgCl/NaCl$ in $W/gas/NaCl$ in $S/AgCl/Ag$ (B)

The e.m.f. E_A measured in cell A is related to the "real" standard molar Gibbs energy $\alpha_{Ag^+}^\infty$ of the silver ion by

$$FE_A = [\alpha_{Ag^+}^\infty(S) + RT \ln a_{Ag^+}(S)] - [\alpha_{Ag^+}^\infty(W) + RT \ln a_{Ag^+}(W)]$$ (1)

where F is the Faraday constant and a the thermodynamic activity. This quantity is the product of the concentration of the silver ion and its activity coefficient. A suitable

expression for the ratio of the single ion activity coefficient in each of the solvents W and S is required in order for $\alpha_t^\infty(Ag^+, W \to S)$ to be evaluated. This, then, requires an extrathermodynamic assumption, and it is customary to evaluate these activity coefficients from some variant of the Debye-Hückel equation, e.g.:

$$\ln \gamma_i(S \text{ or } W) = -\underline{A}(S \text{ or } W)\underline{z}_i^2\underline{I}^{1/2} \, [1+\underline{B}(S \text{ or } W) \, \underline{a}^0_i\underline{I}^{1/2}]^{-1} \qquad (2)$$

Here the coefficients $\underline{A}$ and $\underline{B}$ are known functions of the temperature and of the relative permittivity of the solvent concerned, $\varepsilon(S \text{ or } W)$, $\underline{z}_i$ is the charge on the ion, $\underline{a}_i$ is taken as a solvent-independent characteristic parameter of the ion, and $\underline{I}$ is the ionic strength. It must be pointed out that the ratio of single ion activity coefficients (in two solvents) approaches unity on the diminution of the concentration of the electrolyte faster than each individually. This fact tends to decrease the errors possibly introduced by the estimates of the activity coefficients, when extrapolation of $\underline{E}_A$ with respect to the concentration of the salt is carried out, to yield $\underline{E}_A^\infty$.

The difference between the "real" standard molar Gibbs free energies is given by

$$\alpha_{Ag^+}^\infty = \underline{F} \lim [\underline{E}_A - \ln(\underline{m}_{Ag}(S)/\underline{m}_{Ag}(W)] \qquad (3)$$

The "real" standard molar Gibbs free energy of the ion i in the solvent S is related to its standard chemical potential $\mu_i^\infty(S)$ by

$$\alpha_i^\infty(S) = \mu_i^\infty(S) + \underline{z}_i\underline{F}\chi(S) \qquad (4)$$

and similarly for i in W. Here $\chi(S)$ is the surface potential of the solvent against the gas used in the gap between the solution streams. It follows that
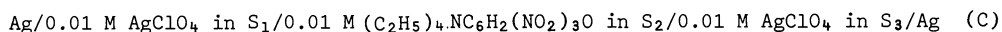
$$\Delta\underline{G}_t^\infty(Ag^+, W \to S) = \Delta\alpha_t^\infty(Ag^+, W \to S) + \underline{F}\Delta\chi \qquad (5)$$

The difference in surface potentials, $\Delta\chi = \chi(S) - \chi(W)$ must still be estimated in order to obtain from the measurements of the compensating voltage $\underline{E}_A$ the standard molar Gibbs free energy of transfer. Estimates of $\Delta\chi$ have been given for $\overline{S} =$ methanol or ethanol, based essentially on other methods for the estimation of $\Delta\underline{G}_t^\infty$. The limits of uncertainty estimated for $\chi(W)$ are ± 0.1V, those for $\chi(\text{methanol})$ are ± 0.13 V. These correspond to ±10 and ±13 kJ mol^{-1} in $\Delta\underline{G}_t^\infty$, respectively. The most direct method for estimation of $\Delta\chi$ is the one that was applied to S = acetonitrile.[9] For several multinuclear aromatic hydrocarbons (such as anthracene or pyrene), the charge distribution and the size are nearly the same for the positive and negative ions produced on oxidation or reduction. If, for such ions, the assumption $\Delta G_{solv}^\infty(+\text{ve ion}) = \Delta G_{solv}^\infty(-\text{ve ion})$ is made, the mean values of $\chi(\text{acetonitrile}) = -0.10 \pm 0.06$ V is obtained for half a dozen of such ionized large aromatic hydrocarbons. The relative constancy of $\chi(\text{acetonitrile})$ speaks for the validity of the assumption.[9]

To summarize, the use of the "real" potentials for the estimation of $\Delta\underline{G}_t^\infty(i, W \to S)$ depends on the proper selection of expressions for the activity coefficients of ions in the two solvents W and S and on an estimate of the surface potential between them. For the latter quantity, an assumption of category g) has been proposed, so that altogether the category a) method does not seem to be an independent one.

(b) A negligible liquid junction potential has been assumed long ago[13] to exist when a 3.5 M (M = moL dm^{-3}) aqueous KCl calomel reference electrode is used in aqueous, ethanolic, or mixed aqueous-ethanolic solutions. The well documented and supported partial suppression of the liquid junction potential between two rather similar dilute aqueous solutions by means of the 3.5 M aqueous KCl salt bridge is by virtue of the high concentration and nearly equal mobilities of K$^+$ and Cl$^-$ ions in this bridge solution. The presumed extension of this to nonaqueous and mixed media was a mere assumption, however. Its validity was tested[13] only by a comparison of the consequences of this assumption with results obtained by a method from category c), which was not necessarily trustworthy.

A revival of this kind of assumption was made later,[14,15] in the suggestion that 0.1 M tetraethylammonium picrate could make a suitable salt bridge in any solvent, as it practically eliminates the liquid junction potential. It is supposed to do so by virtue of the "inertness" and similar mobilities of the constituent ions. This assumption is supported by the fact that the e.m.f. is virtually independent of the nature of the bridge solvent S_2 in cells of the type

$$Ag/0.01 \text{ M } AgClO_4 \text{ in } S_1/0.01 \text{ M } (C_2H_5)_4.NC_6H_2(NO_2)_3O \text{ in } S_2/0.01 \text{ M } AgClO_4 \text{ in } S_3/Ag \qquad (C)$$

The solvent S_2 can be either the same as one of the solvents S_1 or S_3 or a different one altogether. Both protic and polar aprotic solvents can be separated with such a salt bridge and a practically constant e.m.f. is produced. For $S_1 =$ acetonitrile and S_2 being almost any

one of ten solvents tested, the mean e.m.f.'s are -0.155 ± 0.005 V for S_3 = dimethylsulfoxide, 0.066 ± 0.008 V for S_3 = formamide, 0.182 ± 0.023 V for S_3 = water, and 0.262 ± 0.009 V for S_3 = methanol. The same appreciable liquid junction potential could hardly occur with bridge solvents S_2 as diverse as acetonitrile, dimethylsulfoxide, nitromethane, methanol, acetone, N,N-dimethylformamide, and formamide. Hence it was concluded that, within the standard deviations quoted, the liquid junction potential was negligible. Apart from the case of transfer between acetonitrile and water, the above error limits correspond to only ± 0.7 kJ mol^{-1} in ΔG_{-t}^{∞}, in the case of transfer to water to ± 2.2 kJ mol^{-1}. In every case, however, there was one or more non-conforming bridge solvent (e.g., S_2 = formamide for S_3 = dimethylsulfoxide, S_2 = dimethylsulfoxide, N-methylpyrrolidinone, and N,N-dimethylformamide for S_3 = formamide), that cause larger errors, especially in the case of S_3 = water.[15]

In conclusion, the negligible liquid junction potential assumed with a 0.1 M tetraethyl-ammonium picrate salt bridge is convenient to apply to cell e.m.f. measurements of good accuracy. The main drawback of this extrathermodynamic assumption is its completely empirical nature, making it necessary to examine each new solvent S_3 in cell (C) separately with a group of bridge solvents S_2 to establish its applicability. The main problem is its partial failure with particular solvents, the nature of which cannot be foreseen.

(c) Electrostatic models have often been used for the calculation of the work done on the transfer of an ion from one solvent to the other. The Born equation gives the electrostatic work:[13]

$$\Delta G_{-t}^{\infty}(i, W \rightarrow S)_{el} = (1/8\pi) \underline{N}_{Av} \underline{z}_i^2 \underline{e}^2 \varepsilon_o^{-1} [(\underline{r}_{i,s} \varepsilon_s)^{-1} - (\underline{r}_{i,w} \varepsilon_w)^{-1}] \tag{6}$$

where $\underline{N}_{Av}$ is Avogadro's constant, $\underline{e}$ is the unit charge and ε_o is the permittivity of vacuum. In general, the radii of the ion in the two solvents are taken to be equal: $\underline{r}_{i,s} = \underline{r}_{i,w}$. The crystal ionic radius is often used for $\underline{r}_i$ in both solvents and the bulk relative permittivities ε_s and ε_w of the solvents are employed. Then, however, the sum of the calculated quantities $\Delta G_{-t}^{\infty}{}_{el}$ for a cation and an anion does not yield the measured ΔG_{-t}^{∞} of the corresponding electrolyte. Equation (6) requires, therefore, modification in order to provide acceptable ΔG_{-t}^{∞} values for ions.

The first modification, proposed long ago,[13] involved the addition of a "neutral term" to the electrostatic term given by eq. (6). This term should express the difference in the work required to produce a cavity in the solvents W and S for the accommodation of the transferred ion. It should also express the unequal compensation of this work by the non-electrostatic interactions (dispersion) of the ion with these solvents. The experimental distribution ratio $\underline{D}$(neut, S/W) of the isoelectronic neutral analog of the ion (e.g., Ar for K^+ or Cl^-, benzoic acid for the benzoate ion) was used[13] to provide this term:

$$\Delta G_{-t}^{\infty}(i, W \rightarrow S)_{neut} = \underline{RT} \ln \underline{D}(neut, S/W) \tag{7}$$

The sum of $\Delta G_{-t}^{\infty}{}_{el}$ and $\Delta G_{-t}^{\infty}{}_{neut}$ should be a better approximation than $\Delta G_{-t}^{\infty}{}_{el}$ alone for the individual ionic ΔG_{-t}^{∞}. The neutral solute may be sought not as the isoelectronic analog of the ion, but as a particle of the same radius. This can be obtained by interpolation in the (almost) linear plot of $\ln \underline{D}$(neut, S/W) against $\underline{r}_{neut}^2$ for a series of noble gas or other nonpolar solutes.[16]

A major difficulty with this treatment arises from the fact that dielectric saturation sets in near the ion for ions as small as the crystal ionic radius implies. Thus the bulk relative permittivity is not the appropriate quantity to be used in the electrostatic expression (6). Either the radii $\underline{r}_{i,s}$ and $\underline{r}_{i,w}$ or the relative permittivities ε_s and ε_w or both pairs of quantities must be modified to take this effect into account. Various schemes have been proposed for this purpose,[3] but due to the lack of quantitative information concerning the effect of the ionic field on the dielectric saturation in nonaqueous solvents, most of the schemes have tackled the ionic size instead. In the most useful scheme a quantity is empirically added to $\underline{r}_i$, individually for the two solvents W and S. In eq. (6) each $(\underline{r}_i \varepsilon)^{-1}$ is replaced by $(\underline{r}_i + \Delta r)^{-1}(1 - 1/\varepsilon)$, where Δr is the same for all cations (only the alkali metal cations have been considered) and has another value for all anions (only the halide anions have been considered) in a given solvent.[17]

In the implementation of this approach, the necessity of the inclusion of a "neutral term" as discussed above was ignored and Pauling crystal ionic radii were used for $\underline{r}_i$. Then for water Δr_+ = 0.079 nm and Δr_- = 0.039 nm, for acetonitrile Δr_+ = 0.072 nm and Δr_- = 0.061 nm, and so on. These values were selected empirically so that the deviation of the calculated $\Delta G_{-t}^{\infty}{}_{el}$ from the experimental ΔG_{-t}^{∞} for an electrolyte was divided equally between the largest ions considered, Cs^+ and I^-.[17,18] Different choices of the addends are, however, equally plausible. For instance, $\underline{r}_+$ = 0.072 nm and $\underline{r}_-$ = 0.045 nm were suggested for water,[19] which then yield different values for the solvents S, e.g., Δr_+ = 0.082 nm for acetonitrile and Δr_+ = 0.074 nm for acetone. This indefiniteness may possibly be due to the disregard of $\Delta G_{-t}^{\infty}{}_{neut}$ in the procedure.

More elaborate electrostatic models for the Gibbs energy of solvation of ions in solvents have been proposed by other authors. Noteworthy is a formulation that takes into account not only a Born-type term, eq. (6), and a neutral term, but also ion-dipole, ion-quadrupole, etc., interaction terms.[20-22] The difficulty with this approach is that the coordination number of the ion and the quadrupole moments of the two solvents are required, but are available from independent sources only in exceptional cases. As applied in practice, these quantities were treated as fitting parameters, and this introduces a large degree of arbitrariness and uncertainty.

It is seen, in conclusion, that this modelling attempt involves a number of arbitrary choices, such as the addends to the ionic radii in the electrostatic term and, if used at all, the neutral analog of the ion for the neutral term. It is unlikely that a compelling theoretical breakthrough will be made in this regard, and even for the reference solvent, water, these quantities (pertaining to $\Delta G^{\infty}_{-hydr}$) are not definitely known. A comparable success with nonaqueous solvents is even less likely.

(d) Extrapolation methods also employ models, in which $\underline{G}^{\infty}_{-t}$ of a series of electrolytes with a common ion are plotted against the reciprocal of a smoothly varying quantity characterizing the counter-ion. The curve is then extrapolated to an infinitely large size (zero value of the reciprocal) of the latter. In its more primitive form, this method has been applied to the alkali halides and hydrohalic acids.[23] The quantities characterizing the counter ions are either some power of the crystal ionic radius, $\underline{r}_{ip}$ ($\underline{p}$ = 1, 2, 3, 4, or 6) or the square of the main quantum number, $\underline{n}^2$. These two kinds of extrapolation give discordant values to the extent of 4 to 6 kJ mol^{-1}, and that against $\underline{n}^2$ has been considered as the more reliable.[23]

This approach runs into the difficulty that a neutral term is generally considered as essential in the electrostatic modelling dealt with in category (c). That term should then also be added in the extrapolations that implicitly are based on such an electrostatic model. However, the neutral term depends on a positive power of the ionic radius, so that the extrapolation to $(1/\underline{r}_i) = 0$ necessarily diverges to infinity.

In a more sophisticated approach[20,21] this difficulty is dealt with by first subtracting a calculated neutral term, before making the extrapolation. The extrapolation is carried out either with the crystal ionic radius, or with its sum with the diameter of the solvent molecules in different versions of this method.[20,24] One of these made an extrapolation not of the ΔG^{∞}_{-t} of electrolytes (i.e., the sum of the values of the cation and anion) but of the difference in the $\Delta G^{\infty}_{-solv}$ of cations and anions of equal radius in a given solvent. "Conventional" values, i.e., those obtained assigned on the basis of the additivity principle and an arbitrarily assigned value to one ion (H^+), were first plotted against the reciprocal of the Gourary and Adrian crystal ionic radii, producing strongly curved lines. When the difference was taken, however, a nearly linear curve resulted for the two solvents examined: water and propylene carbonate. Their difference, in turn, permitted ready extrapolation to $(1/\underline{r}_i) = 0$. The basis for the choice of $\underline{r}_i^{-1}$ for extrapolation was a presumed compensation effect of the enthalpy and entropy of solvation.[24]

The extrapolation methods do not provide a sound theoretical basis for the selection of the property of the counter ion (the value of $\underline{p}$, the power of $\underline{r}_i$) against which the ΔG^{∞}_{-t} of electrolytes (or sums or differences of them) should be plotted. The more sophisticated approaches involve a host of unknown coefficients, including an estimate of the neutral term. This is wrongly omitted in the simpler approach, but is not known definitely enough.

(e) The reference ion assumption considers ΔG^{∞}_{-t} (i_R, W → S) of a judiciously selected reference ion i_R to be the same for all solvents S. In order to fulfill this requirement i_R should be not so large that differences in the work of the creation of a cavity for its accommodation in various solvents ensue, but sufficiently large to be only poorly solvated. These two requirements are contradictory, and it is, therefore, impossible in principle to find such a reference ion.

On the practical side, it was once considered that Rb^+ might fill this role of i_R.[25] It soon transpired, however, that it is not sufficiently large ($\underline{r}_i$ = 0.148 nm) for differences in its solvation not to be manifested. On the basis of the extrathermodynamic assumption that is considered (see below) to yield ΔG^{∞}_{-t} (i, W → S) values nearest the true ones, within ±2 kJ mol^{-1}, the values obtained range from ΔG^{∞}_{-t} (Rb^+, W → ethanol) = 16 kJ mol^{-1} to ΔG^{∞}_{-t} (Rb^+, W → dimethyl sulfoxide) = -10 kJ mol^{-1} for the most commonly considered solvents.[5,6] The "Pleskov" or "Rubidium" assumption is, therefore, untenable.

The assumption ΔG^{∞}_{-t} $[(CH_3)_4N^+$, W → S$]$ = 0 was proposed[26] on a "conventional" rather than an "absolute" basis. This means that it was not claimed that the assumption was true, only that the experimentally measurable quantity ΔG^{∞}_{-t} (i^+, W → S) - ΔG^{∞}_{-t} $[(CH_3)_4N^+$, W → S$]$ (e.g., from the relative solubilities of salts with common anions) could serve as a convenient "conventional" substitute for the "absolute" value of ΔG^{∞}_{-t} i^+,W → S . This expectation turns out, in fact, not to be very wrong: the deviations are generally within 5 kJ mol^{-1}.

A more sophisticated idea is behind the use of a chelating ligand that "screens" the reference ion from interactions with its environment. The cryptand (221) = tricyclo-N,N'-bis (3,6-dioxa-1,8-octadiyl)(3-oxa-1,5-pentadiyl) envelops an alkali metal cation such as Na^+ completely. The cryptated cation has been assumed not to contribute to ΔG_t^∞ of the electrolyte.[27] Therefore, Na(cryptand)$^+$ is a reference ion with ΔG_t^∞ (i_R, W → S) = 0. This idea was tested on very few systems only, because of the laborious vapor pressure measurements required. Although promising, the results were inconclusive.

The problem of the non-negligible work of cavity formation that may differentiate among solvents and produce nonzero ΔG_t^∞ (i_R, W → S) even for a "nonsolvated" ion has also been tackled.[28] This approach sets $[\Delta G_t^{\infty R}(i_R$, W → S) - ΔG_t^∞ (ligand, W → S)] = 0, with the ligand (222) = tricyclo-N,N'-tris(3,6-dioxa-1, 8-octadiyl). This cryptand should give similar results to those obtained with the cryptand (221),[27] as indeed it gave. Again, however, the testing was not very extensive, although a convenient electrometric method was used. This promising approach bears some resemblance to method (f) discussed below, and some of the drawbacks of the latter should pertain to the present method too. In fact, subsequent testing by other investigators[67,68] revealed instances where the expected shielding of the metal cation by the cryptant was not achieved. Thus, ΔG_t^∞ (ClO_4^-), W → W + MeCN) should be independent of the accompanying cation, whether K^+ or Ag^+, if it is shielded completely by the cryptand 222, but discrepancies up to 5.7 kJ mol^{-1}, for transfer into pure acetonitrile, were found. [67] A more extensive examination of this cryptand and K^+, Ag^+, and Tl^+ showed good shielding only for the transfer between two aprotic dipolar solvents. For transfers from water ΔG_t^∞ ($i_R L^+$, W → S) - ΔG_t^∞ (L, W → S) ≠ 0 but still independent of the cation, except for transfer into methanol where it depends on the particular cation used. Similar results were obtained when other cryptands were employed, such as 211, 221, or the monocyclic 21 and 22, and when divalent cations were used, such as Pb^{2+}, Cu^{2+}, and Cd^{2+}, for transfer to methanol, propylene carbonate, and dimethyl sulfoxide.[68] It must be stressed, however, that these results are derived from the equilibrium constants for $M^+ + L = ML^+$ in the two solvents, where the standard Gibbs free energy of transfer of M^+ was obtained by means of the TATB assumption of category (g), see below. Although this method is recommended at present as the least objectionable extrathermodynamic assumption, its use in the present context cannot be taken with the above results, as proof of the nonvalidity of the cryptand method.

Crown ethers (e.g., eicosahydro-dibenzo-2,5,8,15,18,21-hexaoxacyclooctadecin, i.e., dicyclohexo-18-crown-6), admittedly, envelop alkali metal ions less completely than do cryptands. They may, indeed, permit interactions with solvent molecules or anions located along an axis perpendicular to the plane of the crown ether. This was demonstrated[66] by the comparison of log γ_t^∞ (KL$^+$, MeOH → S) with log γ_t^∞ (L, MeOH → S), where γ_t^∞ = exp (ΔG_t^∞/RT), for the ligand L = dibenzo-30-crown-10. Only for S = MeCN was near equality found, whereas discrepancies up to 1.3 units were found for other solvents. It was shown empirically, however, that the distribution of KCl between a dilute aqueous solution and a suitable crown ether in a variety of water-immiscible solvents can be used for the evaluation of ΔG_t^∞ (Cl$^-$, W → S). The distribution ratio yielded the value of the equilibrium constant, hence the corresponding Gibbs free energy change, ΔG_{distr}^∞(KCl, S/W), a semiempirical relation related this to the transfer of the chloride ion:[29,30]

$$\Delta G_t^\infty \text{ (Cl}^-\text{, W → S)} = G_{distr}^\infty \text{(KCl, S/W)} + A + B/\varepsilon_s \qquad (8)$$

where A = 29 kJ mol^{-1} and B = 116 kJ mol^{-1}. The last two terms on the right hand side represent $-\Delta G_t^\infty$ (K$^+$(crown), W → S). If the potassium cation were completely shielded by the ligand, then B would presumably be zero (and A would have a larger value, representing the transfer of the crown ether). As it is, the finite value of B takes into account the imperfect shielding of the potassium cation by the crown ligand. This method is limited to transfers to water immiscible solvents, however, due to the required distribution measurements.

In conclusion, it seems that the reference ion method can be accepted, provided effective shielding of this ion from all solvents can be achieved. Another provision is that the "neutral term" is adequately taken into account. The approaches suggested for its realization, however, were either limited by the experimental methods that had been used, or not tested over a sufficiently wide range of solvents.

A subcategory of the reference ion approach involves specifically the hydrogen ion. If a large neutral molecule can be protonated without otherwise changing its solvation properties, then presumably a comparison of the transfer Gibbs free energy of this molecule and its protonated form could form the basis for an extrathermodynamic assumption concerning the transfer of individual ions.

An early reduction of this idea to practice involved the Hammett acidity function H_o. This is measurable with the so-called Hammet indicators, i.e. nitro- and/or halo-substituted anilines.

In aqueous acid solutions $\underline{H}_o$ is independent (within < 0.05 units) of the particular indicator employed, due to the cancellation of activity coefficient effects. The transfer activity coefficient of the hydrogen ion is

$$\log \underline{y}_t^\infty \ (H^+, \ W \rightarrow S) = -\underline{H}_o - \log \underline{c}_{H^+,S} - \log \underline{y}_{H^+,s} + \log \ (\underline{y}_{SH^+,s}/\underline{y}_{B,s})$$

$$+ \log \ [\underline{y}_t^\infty \ (BH^+, \ W \rightarrow S)/\underline{y}_t^\infty(B, \ W \rightarrow S)] \tag{9}$$

where $\underline{H}_o = \log \ [(B)/(BH^+)] + pK_{BH^+}$ is obtained spectrophotometrically by employing the indicator B. The quantity $\underline{y}_{H^+,S}$ is generally unknown hence set equal to unity in dilute solutions. The quantity $(\underline{y}_{BH^+,S}/y_{B,S})$ is set equal to unity because of the presumed similarity in size of the protonated and unprotonated forms of the indicator B. For this reason also the ratio of their transfer activity coefficients is set equal to unity. Therefore, eq. (9) gives an approximate value of $\underline{y}_t^\infty \ (H^+, \ W \rightarrow S)$ from the measured $\underline{H}_o$ and $\underline{c}_{H^+}$. This approach was applied mainly to mixed aqueous-alcoholic media. The required assumptions are unsatisfactory, however,[3] not the least because of the fact that whereas substituted anilines and anilinium ions are large, the charge is effectively localized on the small $-NH_3^+$ group that interacts strongly with its surroundings.[18]

A more elaborate approach was again applied to mixed aqueous-organic media, but was wisely limited to the water-rich part of the composition range.[31,32] The hydrogen ion in aqueous solutions was assumed to be the tetrahedral species $H_3O(H_2O)_4^+$, which was approximated by a sphere with a radius $\underline{r}_{H^+,aq} = 3 \ \underline{r}_{H_2O} = 0.414$ nm. This was assumed to be sufficiently large for the bulk relative permittivity to apply in the Born equation (6) for both the aqueous and the mixed aqueous-organic media. The electrostatic term is, therefore,

$$\underline{\Delta G}_{t,el}^\infty \ (H^+, \ W \rightarrow S) = (1/8\pi)\underline{N}_{Av}\underline{e}^2\varepsilon_o^{-1}(3 \ \underline{r}_{H_2O})^{-1} \ (\varepsilon_s^{-1} - \varepsilon_w^{-1}) \tag{10}$$

A proton exchange term was calculated from the equilibrium constant

$$\underline{K}_{exch} = (SH^+)[(W)_o-(S)_T]/[(H^+)_T-(SH^+)][(S)_T-(SH^+)] \tag{11}$$

where $(W)_o = 55.5$ M is the concentration of water in the absence of the cosolvent S. The amounts with subscript T are the total concentrations of the cosolvent S and acid. The amount of proton exchange that had taken place per unit concentration of H^+ was (SH^+). Hence $\underline{\Delta G}_{t,exch}^\infty(H^+, \ W \rightarrow S) = (SH^+)(-RT \ln \underline{K}_{exch})$. The concentration (SH^+) was determined by means of a Hammett-acidity-function-type experiment with 4-nitroaniline as the indicator. This procedure involved two assumptions: that the concentrations of unprotonated water in the presence and absence of the cosolvent S were essentially the same, and that the activity coefficient ratio $\underline{y}_{BH^+} \ \underline{y}_{H_2O}/\underline{y}_B\underline{y}_{H^+,aq}$ was unaffected by the presence of S.[31,32] This limits the applicability of this approach to very water-rich mixtures since these assumptions are tenable only if the concentration of S is very small. The other assumptions, concerning the electrostatic term, need be valid too for the method to be applicable, but this is rather questionable.

(f) The reference ion/molecule redox couple assumption involves an ion that can be oxidized (or reduced) to a neutral species of essentially the same size and structure. The interactions of the ion and the neutral molecular species with any solvent should be the same for a large and symmetrical ion, except for a presumably small electrostatic interaction term for the ion, absent for the molecule, that is neglected. The reference ion/molecule method that has been most widely used involves complexed metal ions in two oxidation states. The e.m.f. of a cell such as (D), in which the redox couple constitutes the reference electrode is measured.

$$Ag/AgClO_4 \ (\text{in W or in S}), \ red, ox^+ \ (\text{in water or in S})/Pt \tag{D}$$
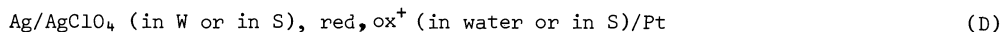
Here 'red' and 'ox$^+$' are examples of the reduced state of the metal complex, which is uncharged, and the corresponding oxidized form. The other electrode is reversible to the ion i, of which $\underline{\Delta G}_t^\infty \ (i, \ W \rightarrow S)$ is to be estimated. When the cell solvent is W in one experiment and S in another, then

$$\underline{\Delta G}_t^\infty(i, \ W \rightarrow S) = \underline{F}(\underline{E}_S^\infty - \underline{E}_W^\infty) \approx \underline{F}(\underline{E}_{e \ S} - \underline{E}_{e \ W}) \tag{12}$$

where $\underline{E}_e$ is the polarographically determined half-wave potential. This quantity is a sufficiently good approximation for the standard e.m.f. $\underline{E}^\infty$. For the most frequently used reference couples W = water happens to be a poor reference solvent, from the standpoints of solubility and electrochemical stability. Acetonitrile is the reference solvent usually preferred.

A variant of the method, involving two ions of different charge, e.g. tris(4,7-dimethyl-1,10-phenantrolino)iron(II) and -iron(III), was used[33] many years ago. The electrostatic contribution to $\Delta G^{\infty}_{\underline{t}}$ is proportional to the square of the charge on the ion, hence the discrepancy between the contributions of $[Fe(DiMephen)_3]^{2+}$ and $[Fe(DiMephen)_3]^{3+}$ is considerably larger than would be obtained from a singly charged/uncharged couple. Such highly charged couples have, therefore, been abandoned since that time.

The criteria for the choice of the singly charged ion and the uncharged molecule that constitute the ideal redox couple are:[19] a large size and nearly spherical shape and an invariant structure on oxidation and reduction. The redox equilibrium must be established reversibly and rapidly. The limits of the allowable redox potential are such, that the solvent is neither oxidized nor reduced by the constituents of the redox couple. Among the redox couples that have been examined, the so-called 'fic$^+$/foc' one due to Strehlow, i.e., dicyclopenta-dienyl-iron(III)(ferricinium)/-iron(II) (ferrocene),[18] has gained wide acceptance. The corresponding cobaltocene couple[18] and the bis(biphenyl)chromium(0)/-chromium(I) couple[34,35] have also been used. The suitability of the 'fic$^+$/foc' couple, the so-called "Strehlow Assumption," stems from its near approach to the criteria listed above. Some apprehensions have been voiced, however, regarding the insufficiently large size of the species involved. The dimensions of ferrocene are 0.51 nm across the rings and a 0.40 nm thickness. These correspond to a mean radius of only 0.23 nm. The electrostatic contribution for the relatively small 'fic$^+$' ion is, thus, not negligible. With the mean radius given, the Born expression eq. (6), gives for transfer from water to a solvent with $\varepsilon_s = 10$ an electrostatic contribution of 26 kJ mol^{-1}, and even for transfer to a solvent with $\varepsilon_s = 40$ this is still 4 kJ mol^{-1}. Some specific solvation of the iron atom between the two "covers" of the "sandwich" complex seems to be possible too. This criticism should apply to all the "sandwich" complexes considered.

Since the contributions of the reduced and oxidized forms to $\Delta G^{\infty}_{\underline{t}}$ do differ by the electrostatic term for 'fic$^+$', that is absent for 'foc', the 'fic$^+$/foc' assumption is at best limited to transfers between solvents of similar relative permittivities. If acetonitrile is used as the reference solvent W, then the solvents S to which the method can presumably be reliably applied should have $30 \leq \varepsilon_s \leq 45$ (see the   partial list). This limitation does not answer the alleged specific solvation of the iron atom in between the covers of the "sandwich."

Although widely applied, the reference ion/molecule redox couple method was not tested adequately with respect to the additivity criterion of cationic and anionic $\Delta G^{\infty}_{\underline{t}}$ data to give the observable quantities for complete electrolytes. An exchange of the perchlorate anion for the nitrate one in cell D should not change the $E^{\infty}_{\underline{S}} - E^{\infty}_{\underline{W}}$ values, if the potential of the 'fic$^+$/foc' reference electrode is solvent-independent. The same should apply to other anions that yield soluble silver salts, e.g., fluoride. Also other anions could be tested, if the silver electrode were exchanged for another reversible electrode that involves cations yielding soluble salts with, say, halide ions. Unfortunately, such tests have not been performed.

(g) The reference electrolyte assumption states that $\Delta G^{\infty}_{\underline{t}}$ should be divided equally between the univalent cation and anion of an electrolyte that are large, spherical, have an "inert" surface, and are equal in size. This equality should be true for the contributions to $\Delta G^{\infty}_{\underline{t}}$ from cavity formation work and dispersion and similar interactions, i.e., $\Delta G^{\infty}_{\underline{t} \, neut}$. This should also hold for the major components of $\Delta G^{\infty}_{\underline{t} \, el}$: the Born charging and the ion-dipole interactions, since these are independent of the sign of the charge on the ion. A minor contribution to $\Delta G^{\infty}_{\underline{t} \, el}$ arises from ion-quadrupole interactions and changes sign when the charge of the ion is flipped from positive to negative. Hence, this latter contribution is not the same for the cation and anion[36] and should lead to an unequal division of $\Delta G^{\infty}_{\underline{t}}$.[37] This contribution is expected not to exceed 10% of $\Delta G^{\infty}_{\underline{t} \, el}$ for large ions.

If the ion-quadrupole interaction is disregarded for the moment, the plausibility of the reference electrolyte assumption is evident. It is difficult to imagine reasons for differing interactions with the solvent of large, spherical cations and anions of equal size that have an "inert" surface. (See, however, the comment further below regarding hydrogen bonding in protic solvents). Note that it is not claimed that the interactions that each kind of ion undergoes are small, only that they are equal is claimed: although $\Delta G^{\infty}_{\underline{t} \, el} < \Delta G^{\infty}_{\underline{t} \, neut}$, the latter is appreciable. The problem is thus reduced to the finding of a suitable reference electrolyte, since large ions with a central charge are polyatomic, and these are not strictly spherical.

Near approximations to such ions are provided by the constituents of three electrolytes that have been proposed for the purpose. These are tetraphenylborates of tetraphenylphosphonium (Ph$_4$PBPh$_4$), and arsonium (Ph$_4$AsBPh$_4$), and of tris(3-methyl-butyl)butylammonium (iPn$_3$BuNBPh$_4$). Of these, mainly the second, Ph$_4$AsBP$_4$ has gained wide acceptance. The idea of the reference electrolyte was first suggested with the use of Ph$_4$PBPh$_4$ in connection with vapor pressure

measurements in a solution in 50 mass % dioxane in water, compared with a solution of tetra-phenylmethane in the same solvent.[38] Later, a more convenient solubility method was used by Alexander and Parker,[39] where, for instance, according to the assumption

$$\Delta \underline{G}_{\underline{t}}^{\infty}(Ph_4As^+, \; W \to S) = \Delta \underline{G}_{\underline{t}}^{\infty}(BPh_4^-, \; W \to S) =$$

$$= -\underline{RT} \ln [\underline{s}(Ph_4AsBPh_4, \; S)/\underline{s}(Ph_4AsBPh_4, \; W)] \tag{13}$$

where $\underline{s}$ is the solubility. This should hold, provided that, as in water, the solubility in the solvent S is so small that no activity coefficient corrections are required. If all the three reference electrolytes mentioned above were equally suitable, then $\Delta G^{\infty}(Ph_4As^+) = \Delta \underline{G}_{\underline{t}}^{\infty}(Ph_4P^+) = \Delta \underline{G}_{\underline{t}}^{\infty}(iPn_3BuN^+)$ for transfer from water to any solvent S. For the former two, the differences found are within the experimental errors ($\pm$ 0.4 kJ mol^{-1}) for transfer into methanol, ethanol, or acetonitrile. For the less symmetrical substituted ammonium ion the differences are somewhat larger.[40],[41]

The validity of the Ph_4AsBPh_4 reference electrolyte assumption, often called the "TATB assumption" in the literature, was thoroughly studied and in principle affirmed.[37] Two minor reservations were voiced: one concerned the ion-quadrupole interactions, the other the non-equality of the sizes of the cation and the anion.

The tetraphenyl compounds Ph_4C, Ph_4Si, and Ph_4Ge are possible neutral analogs of Ph_4As^+ or BPh_4^- for transfer into acetonitrile or acetone.[37],[40] The van der Waals volumes $\underline{V}_{vdw}$ (corresponding to the van der Waals radii $\underline{r}_{vdw} = (3\underline{V}_{vdw}/4\pi \underline{N}_{Av})^{1/3}$) are

$$\underline{V}_{vdw}(MPh_4) = 4\underline{V}_{vdw}(C_6H_5^-) + (\underline{r}_{cov}(M)/\underline{r}_{cov}(C)]^3 \underline{V}_{vdw}(-\overset{|}{\underset{|}{C}}-) =$$

$$= 183.36 + 7294.1 \; [\underline{r}_{cov}(M)/nm]^3 \; cm^3 \; mol^{-1} \tag{14}$$

where $\underline{r}_{cov}$ is the tetrahedral covalent Pauling radius. The molar volumes and radii of the tetraphenyl ions and molecules[5] show that Ph_4C is, indeed, the correct analog of BPh_4^-, but that Ph_4Si is a better analog to Ph_4As^+ than is the Ph_4Ge suggested by Kim.[37] The discrepancy in $\Delta \underline{G}_{\underline{t}}^{\infty}$ between Ph_4As^+ and BPh_4^- on account of the size differences is proportional to $\underline{r}_{vdw}^{-1}$ and $\underline{r}_{vdw}^{2}$ for the Born term and the neutral term, respectively. Since $\underline{r}_{vdw}(Ph_4As^+)/\underline{r}_{vdw}(BPh_4^-) = 1.0122$, the discrepancy arising from the size difference is 1.2% and 2.4% in these terms. These are smaller than the estimates of Kim,[37] based on Ph_4Ge as the analog of Ph_4As^+.

There remains the problem of the ion-quadrupole interactions. The difference in $\Delta \underline{G}_{\underline{t}}^{\infty}$ of Ph_4As^+ and BPh_4^- arising from this effect is related to the charge on the surface of the tetraphenyl moeity, the sizes of the solvent molecules, and their quadrupole moments. Its attempted calculation[37] involved too many unverifiable assumptions to be useful. In particular, the values of the quadrupole moments of the solvents used in the calculations (except water) were not obtained from independent measurements. They were, in fact, obtained from fitting electrolyte transfer data! [20-22]

The deviation of the ionic $\Delta \underline{G}_{\underline{t}}^{\infty}$ on account of both the size and the ion-quadrupole inter-action effects from the equipartition value is less than the experimental error in all the cases examined[37] except for acetone and, possibly, N,N-dimethylformamide. On this account, the TATB assumption, i.e., the equal partition of $\Delta \underline{G}_{\underline{t}}^{\infty}(Ph_4AsBPh_4, \; W \to S)$ between its consti-tuent ions, is a good first approximation.

Objections to the TATB assumption have been raised on several accounts. An early objection was due to the inadequate measurability of the solubility of Ph_4AsBPh_4 in water at the time. (That was also an objection for the use of water as the reference solvent.) Indeed, the earlier measurement of the solubility product of Ph_4AsBPh_4 in water at 25°C gave[39],[42] pK_s = 17.2 ± 0.6 (i.e., an uncertainty of a factor of 2 in the solubility). A later more accurate value obtained by activation analysis was[37] pK_s = 17.51 ± 0.21, where the uncer-tainty in the solubility decreased to ± 27%. This uncertainty corresponds to ± 1.2 kJ mol^{-1} in ΔG_t^{∞}, but is, of course, a constant quantity that is independent of the ions and solvents. The problem of the formation of crystal solvates that would obviate solubility measurements for the determination of ΔG^{∞} have been mentioned,[3],[42] but no evidence was produced that they were formed by the reference electrolyte Ph_4AsBPh_4. This is also highly unlikely for a salt with ions having a hydrocarbon-type exterior and the polar solvents usually considered. (Not so for some salts that contain only one of these ions, the counter-ion being inorganic. The salt Ph_4AsCl forms a monohydrate, Ph_4AsBr a hemihydrate,[43] for instance).

Objections to the TATB assumption arising from more direct observations are those based on n.m.r. data.[44],[45] It was found that whereas the n.m.r. signals of the [11]B, ^{31}P, and [75]As atoms in the ions BPh_4^-, Ph_4P^+, and Ph_4As^+ are insensitive to the solvents, the signals from ^{1}H and ^{13}C in the phenyl rings do depend on the solvent. Most sensitive, as may be expected, are the atoms located in the paraposition. A difference in the chemical shift between those of Ph_4As^+ and BPh_4^- (11.4 ppm in water for the p- [13]C) is not inconsistent with the TATB assumption. However a dependence of this difference on the solvent (12.5 ppm in propylene carbonate, 12.7 ppm in nitromethane, 12.9 ppm in dimethylsulfoxide, 13.1 ppm in N,N-dimethyl-formamide) is.[45] Less conclusive was the earlier evidence on the chemical shifts of ^{1}H atoms belonging to the solvent molecules, induced by salts containing these tetraphenyl ions. These depended on the assignment of arbitrary shifts to the Et_4N^+ or the ClO_4^- ions. They led to a dispersion of shift values among the solvents acetonitrile, sulfolane, and dimethylsulfoxide of up to 0.035 ppm for Ph_4As^+, up to 0.067 ppm for Ph_4P^+, and up to 0.133 ppm for BPh_4^-. For hydroxyl protons of the solvents water, methanol, and ethanol, the dispersion ranged up to 0.175 ppm for these cations and 0.40 ppm for the anion.

The problem with these observations is not that they point to specific interactions between the large tetraphenyl ions with particular solvents. Such interactions are granted by the TATB assumption, although not taken into account in the various neutral and electrcstatic interactions considered in the analysis of the validity of the assumption made, e.g., by Kim.[37] In fact, a pictorial presentation[46] of a tetraphenyl ion, Fig. 1, shows that small molecules (in particular water) can penetrate to some distance in between the phenyl groups. The questions are whether the tetraphenyl cations and anions behave differently, and if so to what extent in the energetic sense, pertaining to ΔG_t^∞.

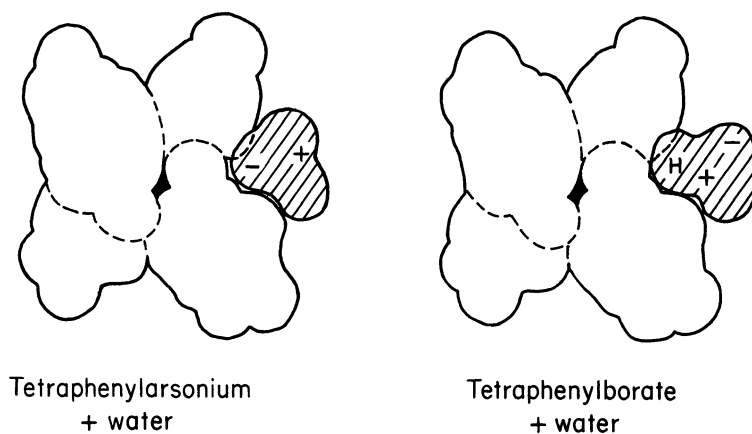Tetraphenylarsonium
+ water

Tetraphenylborate
+ water

Figure 1.   A representation of the near approach of a water molecule to a tetraphenyl-ion (-arsonium on the left, -borate on the right). The black area is the exposed part of the central atom, the shaded area is the water molecule, oriented differently in the two cases.

The first question must be answered in the affirmative, both on grounds of the n.m.r. evidence and on those of the ion-quadrupole interaction and the ion-dipole interactions with solvents that cannot be approximated well by a point dipole. If the negative pole of such a solvent dipole can approach between the phenyl groups to the positive center of the tetraphenyl cation nearer than can its positive pole to the negative center of the anion, a difference in the ion-dipole energetics results. Furthermore, protic solvents are apt to hydrogen-bond to the tetraphenylborate anion, an interaction that is absent with the tetraphenylarsonium cation. Such hydrogen bonding is rather weak, however, as was observed in a study of the crystal structure of ammonium tetraphenylborate.[65]

The answer to the second question is so far not available. Neither experimental measurements nor valid theoretical calculations have been presented on the extent of possible contributions of these effects to ΔG_t^∞ of the two ions of the reference electrolyte of the TATB assumption. (The calculations for the ion-quadrupole interaction[37] have been criticized, both here and elsewhere[5].)

4.4 ASSUMPTIONS CONCERNING THE ENTHALPY OF TRANSFER

The methods for splitting $\Delta \underline{H}_t^\infty$ of electrolytes into the ionic contributions are as varied as those for splitting $\Delta \underline{G}_t^\infty$. However, the most widely used is the reference electrolyte one, specifically the TATB assumption. This was originated for this purpose by Arnett and McKelvey,[47] followed by a great deal of work by Friedman[48] and later by him and his coworkers. A comparison of the results of some of the methods was made.[49] The assumption of a negligible liquid junction potential, with tetraethylammonium picrate as the bridge electrolyte, was found not to yield a sufficiently precise temperature coefficient of the cell e.m.f. The reference electrolyte assumption, specifically that $\Delta \underline{H}_t^\infty$ (Ph$_4$As$^+$, W → S) = $\Delta \underline{H}_t^\infty$ (BPh$_4^-$, W → S) for all solvents S, was recommended instead. It yielded values not deviating much from those obtained from the reference ion/molecule assumption. The latter was tested with tetraphenylmethane vs. either tetraphenylarsonium or tetraphenylborate as well as with the 'fic$^+$/foc' couple.[49]

The electrostatic model was employed to calculate $\Delta \underline{H}_t^\infty$ (i, W → S). The differentiation of the Born equation (6) with respect to the temperature is, by itself, insufficient. However, an addend to the crystal ionic radius (which is temperature independent) may be used to account for the dielectric saturation near the ion. This yields

$$\Delta \underline{H}_t^\infty {}_{el} = (1/8\pi)\underline{N}_{Av}\underline{z}_i^2\underline{e}^2\varepsilon_0^{-1}[(\underline{r}_i + \Delta_s)^{-1}\varepsilon_s^{-1}(1 - d \ln\varepsilon_s/d \ln\underline{T}) -$$

$$(\underline{r}_i + \Delta_w)^{-1}\varepsilon_w^{-1} (1 - d \ln\varepsilon_w/d \ln \underline{T})] \tag{15}$$

It is not self-evident whether the addends used for $\Delta \underline{G}_t^\infty {}_{el}$ are valid also for $\Delta \underline{H}_t^\infty {}_{el}$, since the Δ's are mere empirical fitting parameters. Satisfactory results were not obtained with the application of eq. (15) to transfers into propylene carbonate. This could be due to this reason, or to the non-use of a corresponding neutral term, $\Delta \underline{H}_t^\infty {}_{neut}$.[50]

Standard molar enthalpies of solvation of single ions in nonaqueous solvents can be obtained by an extrapolation method, that is completely analogous to that used for aqueous solutions by Halliwell and Nyburg.[51] The differences between $\Delta \underline{H}_t^\infty$ of ions of equal sizes and opposite charges are given by the ion-quadrupole interactions.[36,52,53] The quantity

$$\Delta \underline{H}_t^\infty (Na^+, W \to S) + (1/2)\Delta \underline{H}_t^\infty [A^-(\underline{r}_A = \underline{r}), W \to S] -$$

$$(1/2) \Delta \underline{H}_t^\infty [M^+(\underline{r}_M = \underline{r}), W \to S] = (1/2) [2\Delta \underline{H}_t^\infty (NaA) - \Delta \underline{H}_t^\infty (MA)] \tag{16}$$

provided values for M$^+$ and A$^-$ of equal radius $\underline{r}$ can be obtained by interpolation. Extrapolation of this quantity against $(\underline{r} + \Delta)^{-3}$ should yield $\Delta \underline{H}_t^\infty$ (Na$^+$, W → S). Alternatively to extrapolation it was suggested[52,53] that the ion-quadrupole interaction terms be calculated one by one, but the required parameters are lacking, as pointed out already in connection with the corresponding calculation for $\Delta \underline{G}_t^\infty$.

The extrapolation and electrostatic model methods are seen not to be able to provide individual ionic $\Delta \underline{H}_t^\infty$ values based on measurements independent of the thermodynamic transfer data themselves. These, obtained for complete electrolytes, are either the temperature coefficient of solubilities or cell e.m.f.'s (polarographic half-wave potentials) or calorimetric data of heats of solution. The latter have been obtained with the greatest accuracy, so far, say ± 0.2 kJ mol^{-1} in the better cases.[54] The value of $\Delta \underline{H}_t^\infty$ is, however, a relatively small difference between rather large numbers. Still, with the accuracy quoted for the heats of solution, $\Delta \underline{H}_t^\infty$ should be obtainable for complete electrolytes to ± 0.3 kJ mol^{-1}. The TATB method recommended[49] for the splitting of this into the individual ionic contributions is estimated to yield errors of < ± 1.0 kJ mol^{-1}, on the basis of the results it gives with the criterion of additivity.

4.5 ASSUMPTIONS CONCERNING THE ENTROPY OF TRANSFER

The methods for splitting $\Delta \underline{S}_t^\infty$ of electrolyte into the ionic contributions depend generally on those applied to $\Delta \underline{G}_t^\infty$ and $\Delta \underline{H}_t^\infty$. The entropy of transfer of electrolytes or ions is commonly derived from these two quantities.

$$\Delta \underline{S}_t^\infty (i, W \to S) = [\Delta \underline{H}_t^\infty (i, W \to S) - \Delta \underline{G}_t^\infty (i, W \to S)]/\underline{T} \tag{17}$$

Care must be taken to use the same method for both quantities that are subtracted in eq. (17), as otherwise incompatibilities may lead to errors.

Some independent methods for the evaluation of $\Delta \underline{S}_t^\infty$ have been proposed. In one, standard partial molar entropies of electrolytes in the nonaqueous solvent S are split into conventional ionic values on the basis of $\bar{\underline{S}}_{H^+}^\infty$ (S) = 0. These values are compared with the corresponding ionic quantities in water. The split is then adjusted so that the values for the cations and those for the anions lie on the same straight line, when plotted against the aqueous quantities.[55] This is equivalent to expressing them with the linear function

$$\Delta \underline{S}_t^\infty \ (i, \ W \rightarrow S) = \underline{a}_s + (\underline{b}_s - 1) \ \bar{\underline{S}}_i^\infty (W) \qquad (18)$$

The constants ($\underline{a}_s$ and $\underline{b}_s$) are specific for each solvent: (0.8, 1.04) for heavy water, (-1.6, 0.64) for formamide, (-5.7, 0.72) for N-methylformamide, (-15.9, 0.79) for N,N-dimethylformamide, (-22.4, 0.82) for ammonia, (-10.9, 0.82) for methanol, and (-16.0, 0.79) for ethanol.[55] The absolute values of $\Delta \underline{S}_i^\infty(W)$ can be obtained from the conventional values according to Conway. The linearity shown by eq. (18) is an empirical observation for the solvents listed. It holds to within ± 1.6 to ± 9 $JK^{-1}mol^{-1}$. There exists no valid theoretical basis for its extension to other solvents. It must be validated for each solvent individually.

A similar method essentially assumes $\underline{b}_s$ of eq. (18) to be solvent-independent. The quantity $(\underline{b}_s-1).\bar{\underline{S}}_i^\infty$ (W) is replaced by an ion-specific constant $-\underline{I}_w$, and the identification $\underline{E}_s = -\underline{a}_s$ is made in eq. (18). The result is[56]

$$\Delta \underline{S}_t^\infty \ (i, \ W \rightarrow S) = \underline{E}_s - \underline{I}_w \qquad (19)$$

The solvent-specific constant $\underline{E}_s$ has the following values (in $JK^{-1} \ mol^{-1}$): ethanol 113, liquid ammonia 146, formamide 71, N-methylformamide 84, N-N-dimethylformamide 134, dimethylsulfoxide 105, acetonitrile 126, and acetone 146. The values for $\underline{I}_w$, in $JK^{-1} \ mol^{-1}$ are: Li^+ 63, Na^+ 50, K^+ 38, Rb^+ 42, Cs^+ 46, $(CH_3)_4N^+$ 113, $(C_2H_5)_4N^+$ 177, $(C_3H_7)_4N^+$ 243, $(C_4H_9)_4N^+$ 297, $(C_6H_5)_4P^+$ 222, $(C_6H_5)_4As^+$ 218, F^- 75, Cl^- 50, Br^- 42, I^- 38, ClO_4^- 38, and $(C_6H_5)_4B^-$ 209. These values of $\underline{I}_w$ are not valid for the transfer of the ions into methanol.[56] This fact warns against the extension of the method to solvents not examined in the original paper, unless specifically validated.

The entropy of transfer of the fic^+/foc couple from water to nonaqueous solvents was studied by the use of a liquid junction consisting of 0.1 mol/dm^3 of tetraethylammonium perchlorate between the hot and cold parts of a nonisothermal electrochemical cell. On the assumption that $d\underline{E}_j/dT = 0$ for the liquid junction potential, $T\Delta \underline{S}_t^\infty$ of the fic^+/foc couple ranged from 6 kJ mol^{-1} for transfer into formamide to 25 kJ mol^{-1} for transfer into nitromethane.[69]

4.6 CONCLUSIONS

Various methods have been examined for the splitting of $\Delta \underline{G}_t^\infty$, $\Delta \underline{H}_t^\infty$, and $\Delta \underline{G}_t^\infty$ of electrolytes, all measurable quantities, into the individual ionic contributions, that are unmeasurable. From the discussions presented above it transpires that the reference electrolyte method is the one that has the strongest conceptual basis. The particular implementation of the reference electrolyte extrathermodynamic assumptions by the TATB assumption has been seen to be reasonable, though not beyond criticism.

It can be argued that the difficulties found or surmised for the assumption that the entire body of interactions of Ph_4As^+ with the solvent equal those of BPh_4^- for all solvents are due to three causes. One is the rather open structure, permitting solvent molecules to penetrate partly between the tetrahedrally arranged phenyl groups to the vicinity of the charge. Another is that the phenyl groups are not sufficiently inert, so that the charge of the ion is not completely "buried" but is partly manifested at its surface. A third is that, in fact, the sizes of the cation and the anion are not equal. The remedy to these ills is to find a reference electrolyte that has spherical, large, and inert ions, as originally prescribed. On paper it is easy to devise such ions as $X(CH_2C(CH_3)_3)_4^\pm$, where the atom X is chosen so that the cation and anion have exactly the same size [perhaps P(V) for the cation and Al(III) for the anion will do]. An even more inert surface might be obtained if the $-CH_3$ groups are changed into $-CF_3$ groups. There remain the "minor" problems of whether electrolytes containing such ions can be synthesized, whether they are stable, and if so, whether they will be at all soluble to an accurately measurable extent in the solvents of interest. It must be remembered that the more inert a solute is and the less it interacts with a solvent, the lower is its solubility in it.

The case for the acceptance of the TATB assumption for $\Delta \underline{G}_t^\infty$ (i, W → S) has been argued in detail in this paper, based on the work of Kim.[37] Some further arguments, concerning not only $\Delta \underline{G}_t^\infty$ but also $\Delta \underline{H}_t^\infty$ and $\Delta \underline{S}_t^\infty$, have been presented by Abraham and Masehzadek.[57] In many cases the compensation effect of $\Delta \underline{H}_t^\infty$ and $T\Delta \underline{S}_t^\infty$ operates, so that $\Delta \underline{G}_t^\infty$ is relatively small compared with either of these quantities. Conflicting results will arise from the application of different methods for obtaining single ion standard molar enthalpies and entropies

of transfer. If, as recommended, the reference electrolyte method, with the specific assumption that ΔG_t^∞ (Ph_4As^+, W → S) = ΔG_t^∞ (BPh_4^-, W → S) for all S is adopted at a given temperature, 25°C, it makes sense not to restrict its validity to this one temperature. Accepting it for all temperatures has as a corollary that ΔH_t^∞ (Ph_4As^+, W → S) = ΔH_t^∞ (BPh_4^-, W → S) and ΔS_t^∞ (Ph_4As^+, W → S) = ΔS_t^∞ (BPh_4^-, W → S) for all S must also be accepted. This is, in fact, recommended, until a method, common to these three thermodynamic functions, is found that is demonstratedly better than the TATB assumption.

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