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Gibbs Energies of Transfer of Anions from Water to Mixed Aqueous Organic Solvents

Yizhak Marcus

Department of Inorganic and Analytical Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel

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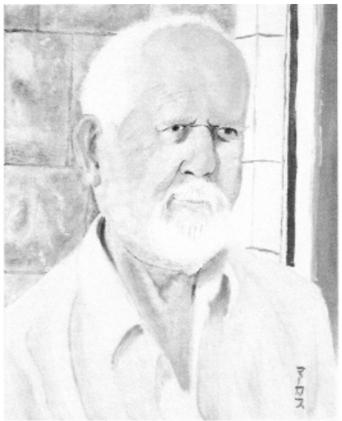

Yizhak Marcus was born in Germany but received all his education in Jerusalem, where he obtained his Ph.D. from the Hebrew University in 1956. He was a researcher at the Soreq Nuclear Research Institute, dealing mainly with actinide chemistry, ion exchange, and solvent extraction. From there he was called in 1965 and appointed Professor of Inorganic and Analytical Chemistry at the Hebrew University. There he taught and did research till his retirement in 1999, but he continues with research as Professor Emeritus. His main interest is solution chemistry: aqueous, nonaqueous, and mixed solvent solutions of electrolytes and nonelectrolytes. He has published in this and neighboring fields 6 books and over 270 papers in refereed journals. Lately, he has taken up painting, and the picture above is of his self-portrait.

1. Introduction

1.1. Gibbs Energies of Transfer and the Solvent Medium Effect

A critical review of the Gibbs energy of transfer (the solvent medium effect) for cations transferring from water into mixed aqueous−organic solvent systems was published by Kalidas, Hefter, and Marcus in this Journal in 2000.[1] The data have been presented in a manner that permits comparison of different cations in a given solvent mixture and of a given cation transferring into different mixtures. It was deemed at the time that insufficient information existed in the literature regarding the corresponding transfer of anions, a consideration that was subsequently found to be erroneous. The present review, therefore, fills this gap with carefully and critically compiled and evaluated anion transfer data, but leans heavily in its scope, format, and the treatment of the data on the former one.

The solvent medium effect is a measure of the change in the total solvation Gibbs energy of a solute i when it is transferred from a reference or source solvent (S_1) to another, the target solvent (S_2), that may be a mixture of solvents. The magnitude of this effect defines the relative stability of the solute in the two solvents and thus the consequences of changing the solvent on equilibria in which the solute is involved, as well as the kinetics and mechanisms of its reactions. As defined, this medium effect is directly related to the standard molar Gibbs energy of transfer of the solute i, $\Delta_t G°(i,S_1 \rightarrow S_2)$, shortened in the following to Gibbs energy of transfer. An older designation, the primary medium effect or activity coefficient (pre-subscript $_m$),

$$ {}_m\gamma°{}_i{}^{S_1}{}_{S_2} = \exp\{[\mu°{}_i(S_2) - \mu°{}_i(S_1)]/RT\} = \exp[\Delta_t G°(i,S_1 \rightarrow S_2)/RT] \quad (1) $$

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is related to the difference in the standard state chemical potentials of i in the solvent (or solvent mixture) S_2 and the reference solvent S_1, on the appropriate concentration scale, but the term "primary medium effect" is of little current use. The "standard" (superscript °) in the quantity $\Delta_t G^\circ$ means that the transfer occurs under the conditions of infinite dilution of the solute in both solvents. This removes any complicating effects of solute–solute interactions.

The reference solvent (S_1) is chosen arbitrarily, but for convenience, especially for the discussion of aqueous/organic mixtures, water is the obvious choice. The choice of concentration scale, on which the numerical magnitude of $\Delta_t G^\circ(\mathrm{i})$ depends, is also optional. Some authors, e.g., Feakins[2] and Popovych,[3] have discussed the solvent medium effect in terms of the molality scale (mol of solute i/kg of solvent S) at a specified temperature and pressure, and others, e.g., Kundu et al.[4] and Wells,[5] have used the mole fraction scale (mol i/[mol i + mol S]). For the reasons given below, the molarity scale (mol solute i/dm^{-3} solution) will be used here, as was done in the previous review.[1] For these reviews, the target solvent S_2 is a selection of mixtures of organic solvents with water over as much of their composition range as possible, i.e., where data are available.

1.2. Significance and Applications of the Medium Effect

The importance of medium effects is far-reaching, since chemical reactions are commonly carried out in solution, many of them involving solvents other than water.[6,7] Solvent mixtures, especially those involving water, are both of fundamental physicochemical interest, with respect to possible preferential solvation, and of considerable practical and technological concern. One advantage of aqueous–organic solvent mixtures over anhydrous nonaqueous solvents is their reduced purification requirements (avoidance of the need for extreme anhydrous conditions), greater ease of manipulation, and lower cost. Another advantage is the ability to tune the solvent composition, and hence its solvation properties, to be used as an additional variable to achieve desired chemical ends.

The present review, dealing with the transfer of anions, is not directly concerned with pH scales in mixed solvents.[1] Nevertheless, the transfer of H^+ ions is of importance in the present context, since many of the experimental transfer data pertain to acids, H^+X^-. Specifically, these data are derived from emf measurements on cells such as

$$\mathrm{GE}|\mathrm{H}^+\mathrm{X}^- \text{ in } \mathrm{S}_1 \text{ or } \mathrm{S}_2|\mathrm{RE} \qquad \text{(I)}$$

where GE is a glass electrode responsive and reversible toward H^+ ions and RE is a suitable reference electrode, e.g., AgX,Ag, with a sparingly soluble salt AgX.

The redox strengths of oxidation–reduction couples in different solvents are of considerable interest for the development of new hydrometallurgical reactions, the rationalization of oxidation state stabilities, etc.[8,9] In principle, it is possible to establish universal scales for electrode potentials by measurements on cells such as

$$\mathrm{Pt, red/ox\ in\ S_1} \,||\, \mathrm{red/ox\ in\ S_2, Pt} \qquad \text{(II)}$$

provided that the liquid junction potential, E_j, at the boundary between the solutions in the two solvents can be estimated reliably in some manner or be rendered negligible. Neither of these options is rigorously possible, with both approaches involving some assumption about the medium effect for single ions. However, if the medium effects for the appropriate ions are known, it becomes possible to estimate E_j. Since galvanic cells with liquid junctions are in practice much more diverse and useful than those without them, such a capability is quite useful.

The medium effect can be used to predict the solubility product K°_{sp} or the solubility of a sparingly soluble electrolyte in one solvent, given its value in another solvent.[10] The role of the medium effect on the kinetics and mechanisms of both organic and inorganic substrates has long been recognized,[11] with the effects usually being greatest for reactions involving charged species. Knowledge of the medium effects and their dependence on charge, size, and other properties of the ions is especially useful when considering the role of the transition state, because such states are generally not amenable to direct study. These applications have been more fully described, and other applications of the medium effect have also been cited in the previous review, the one on cation transfer.[1]

The absolute standard molar Gibbs energies of hydration of many ions have been estimated and are available in standard works.[13] The $\Delta_t G^\circ(\mathrm{i},S_1 \rightarrow S_2)$ values reported here can be added to these to yield the absolute standard molar Gibbs energies of solvation of these anions in the target solvent S_2.

1.3. Scope

The medium effect for the transfer of both cations and anions from water to *neat* solvents has been surveyed in a number of publications, and reasonably comprehensive compilations of the Gibbs energies of transfer are available.[12,13] The transfer of ions into mixed (mainly aqueous/organic) solvents has also been reviewed,[1,14,15] but Waghorne's review[15] was limited in its scope and that of Kalidas et al.[1] dealt only with cations. The review by Marcus[14] was confined to the Gibbs energies of transfer of electrolytes and ions from water to aqueous alcohol mixtures, and considerable subsequent data became available. Thus, the major purpose of the present review is to provide a wide-ranging, critically evaluated compilation of the Gibbs energies of transfer of anions from water to aqueous–organic mixtures. These quantities will then be discussed briefly and interpreted in terms of current views of ion solvation.

The review deals mainly with "simple" inorganic anions, with the halides providing a series of ions of well-defined electronic configuration and systematically varying size, which offers a useful basis for comparison and interpretation. Considerably less information is available regarding other inorganic anions, and information on complex anions is outside the scope of this review. Among the organic anions, only acetate, benzoate ($PhCO_2^-$), picrate (Pic^-), and tetraphenylborate (BPh_4^-) are included, the latter two for reasons to be discussed below.

No attempt is made to be exhaustive with respect to the organic cosolvents, but a fairly large range of solvents for electrolytes, both protic and dipolar aprotic, have been sufficiently well investigated to enable the data to be critically evaluated, as was done previously.[1] However, the lists of cosolvents in the present and the former[1] reviews do not coincide, because of the different availability of data. It must be realized, however, that as the relative permittivity of the aqueous solvent mixture diminishes with increasing organic solvent content, the solubility of electrolytes decreases, as does their degree of ionization. Therefore, the composition range dealt with must be limited to water-rich mixtures for those organic cosolvents that have low relative permittivities ($\epsilon_r \leq 20$) in the neat state.

The data presented pertain to 298.15 K, unless otherwise noted. The literature has been surveyed to the end of 2005.

2. Data Sources and Treatment

2.1. Determination of Medium Effects

The medium effect or the Gibbs energy of transfer of an electroneutral solute or combination of ions can be determined experimentally and has exact thermodynamic significance. The advantages and drawbacks of the more commonly employed and reliable methods for such determinations are briefly outlined here. A more comprehensive discussion of such methods was given earlier.[1]

The thermodynamic relationship

$$\Delta_t G°(C_cA_a,W\rightarrow W+S) = 2.303RT[pK_{sp}°(W+S) - pK_{sp}°(W)] \quad (2)$$

requires the determination of the solubility products $K_{sp}°$ of the salt C_cA_a in the two media. The solubility of the salt should, therefore, be measured at the desired temperature (generally 298.15 K) in the reference solvent, water (W), and the target solvent mixture (W+S). The optimal range of salt solubilities is ca. 10^{-5} to 10^{-2} mol dm^{-3}, permitting accurate determination on the one hand and a reliable estimation of the activity coefficients in the two media and their ratio on the other hand, when the salt is only sparingly soluble.[16] The advantage of the solubility approach is its universal applicability, provided that no crystal solvates are formed. A problem with the solubility method is that it is time-consuming and labor-intensive, since the attainment of equilibrium must be checked by successive measurements, optimally from both above and below saturation, with careful control of the temperature. Reasonable results may, however, be obtained even from solubility measurements of only modest accuracy due to the logarithmic form of eq 2: $pK_{sp}° = -\log K_{sp}°$. It must be remembered that the salt solubility is a characteristic property of a given salt/solvent system at a given temperature. Hence, there exists no freedom of choosing the desirable concentration level, except through a judicious selection of the cation C of the salt C_cA_a in the present context of interest in the anions.

The accuracy and experimental convenience of potentiometry make it a method of wide applicability for the measurement of medium effects.[17] Electrochemical cells of many types can be employed to measure Gibbs energies of transfer, with the choice being limited only by the availability of suitable, reversible, electrodes.[7] Consider, for example, cell III, with one electrode responsive to the cation M^{n+} and the other to the anion A^-:

$$M|MA_n \text{ in W or W+S}|A \quad (III)$$

Measurement of the cell emf, E(III), in the reference and the target solvents as a function of the salt concentration, $c(MA_n)$, permits the determination of the standard emf, E(III)°. This is done by extrapolation to $c(MA_n) \rightarrow 0$ or by calculation, using an appropriate expression for the activity coefficients if the concentration $c(MA_n)$ used is sufficiently low. Then

$$\Delta_t G°(MA_n,W\rightarrow W+S) = nF[E(III)°_W - E(III)°_{W+S}] \quad (3)$$

where F is Faraday's constant. If one of the electrodes employed allows this (e.g., an Ag,AgA electrode), the cells with solvents W and W+S can be coupled back to back, so that the emf of the double cell yields the Gibbs energy of transfer directly. Unfortunately, suitable electrodes cannot always be found, although the situation has improved with the development of ion-selective electrodes, ISEs.[18] Contrary to the case of cation transfer, however, polarography and voltammetry have not found a significant use for the measurement of the Gibbs energy of transfer of anions.

2.2. Single Ion Transfer Thermodynamics

The description up to this point has been applicable to electrolytes, i.e., neutral combinations of cations and anions: acids and salts. It is readily shown that the Gibbs energy of transfer can be determined, in principle, for any electroneutral combination of ions, such as the difference between two cations or two anions of the same charge, e.g., $\Delta_t G°(Br^-) - \Delta_t G°(Cl^-)$. However, the focus of this review is on individual anions, and this involves special problems, because there is *no* thermodynamic method for separating (determinable) electrolyte properties into their ionic components. Nevertheless, though they cannot be measured, these ionic Gibbs energies are widely used for the discussion of the solvation energetics of the individual ions, a practice that is well established.

It has been claimed that the so-called "real" electrochemical potentials can be determined for individual ions by the vertical jet method[19] and, then, via the surface potential difference $\Delta\chi$ between the gas (air) and the solution medium to lead to the ionic standard chemical potentials.[20] However, it was not demonstrated that the resulting measurable electrical potential differences with a cation-selective electrode, e.g., a Na-ISE, are independent of the accompanying anion and that individual ionic "real" electrochemical potentials are thus obtained. The gas/solution surface potentials $\Delta\chi$ are neither known nor determinable very accurately anyway, with the probable error being of the order of 0.05 V, for each solvent, corresponding to ca. 7 kJ mol^{-1} in $\Delta_t G°$. Thus, this route toward the desired individual ionic Gibbs energies of transfer has not ripened to a viable method.

Standard Gibbs energies of transfer imply infinite dilution of the electrolyte; hence, the additivity of the individual ionic contributions is assured. It is, therefore, necessary to fix for a given solvent the value for one ion only; those of all other ions are then obtainable from appropriate thermodynamic cycles. This still requires the use of an appropriate extrathermodynamic assumption. Such assumptions can be checked for self-consistency (precision), but their correctness (accuracy) cannot be determined, although chemical intuition and theoretical understanding can lead to certain preferences. Assumptions leading to $\Delta_t G°(\text{ion},S_1\rightarrow S_2)$ have been reviewed, and their merits have been discussed[1,21,22] and need not be detailed here.

Theoretical considerations show that ions having a low charge-to-radius ratio should have relatively low solvation energies in any solvent, so that the changes in solvation energy should also be minimal when such ions are transferred from one solvent to another. It is now generally accepted that no one ion can have the required solvent-independent properties for all solvents. Therefore, the reference ion assumptions that had sometimes been employed in the past are no longer of significance. Redox couple assumptions, on the other hand, including the ferrocene/ferricinium (Fc)[23] and bisbiphenylchromium(0/I) (BBCr)[24] ones, employed together with electrochemical methods, have been extensively used for the estimation of the Gibbs energy of transfer of cations. The species involved have low charge-to-radius ratios, with the charge being sequestered inside a large organic cage and thereby shielded from direct interaction with the solvent. Thus, despite the inevitable charge difference, the two species of the couple are chemically similar, and thus, their solvation should be relatively little affected by transfer from one solvent to another. However, the electrochemical application of this approach, by means of polarography and similar methods, does not yield the desired information concerning the Gibbs energy of transfer of anions. Nor is the assumption of negligible liquid junction potentials (NLJPs), at least in the manner in which it has been applied, useful for this purpose. This approach assumes that the potential difference, E_j, which develops at the phase boundary between solutions in a galvanic cell such as cell II can be rendered independent of the solvent by separating the solutions in the half-cells with an appropriate salt bridge solution. This procedure, using, e.g., tetraethylammonium picrate in acetonitrile as the salt bridge electrolyte, assumes that its ions have similar electrical mobilities and (low) solvation Gibbs energies in many solvents, leading to $E_j \approx 0$.[25]

The reference electrolyte assumption considers that the (measurable) Gibbs energy of transfer of a suitable electrolyte (C^+A^-) can be divided appropriately between its cation and anion. The electrolyte should have cations and anions with low charge-to-radius ratios that are as chemically similar as possible. Most commonly, the split is even, so that the assumption can be expressed as

$$\Delta_t G°(C^+A^-,W\rightarrow W+S) = 2\Delta_t G°(C^+,W\rightarrow W+S) = 2\Delta_t G°(A^-,W\rightarrow W+S) \quad (4)$$

The salts used most widely for this purpose are tetraphenylarsonium tetraphenylborate (Ph_4AsBPh_4, TATB) and to some extent its phosphorus analogue, tetraphenylphosphonium tetraphenylborate (Ph_4PBPh_4, TPTB). Although the justifications for a slightly unequal split seem reasonable, at least for TATB and less so for TPTB,[26] taking into account small differences in the sizes of the reference ions, the simpler even splitting is used here, as is most commonly done. All extrathermodynamic assumptions for the determination of $\Delta_t G°$(ion) can be objected to on some basis. Careful analysis indicates that the reference electrolyte approach employing TATB or TPTB is based on sound considerations[22,26] and is the least objectionable assumption currently available for the estimation of $\Delta_t G°$(anion,W→W+S) at any mole fraction of S, x_S.

The transfer Gibbs energy of TATB is generally obtained from solubility measurements according to eq 2. Since, however, the solubility of this salt in most solvents, especially aqueous mixtures, is extremely small and barely accurately measurable, recourse is taken to an indirect approach. The solubilities of three salts, such as $KBPh_4$, KPic, and Ph_4AsPic, where Pic is picrate, are readily measurable; their solubility products and Gibbs energies of transfer can therefore be obtained accurately. Those values for Ph_4AsBPh_4 are then obtained by invoking the additivity principle (hence, the relative abundance of $\Delta_t G°(Pic^-)$ and $\Delta_t G°(BPh_4^-)$ values in the compiled data tables). It should be remembered that the reference electrolyte approach employing TATB was the mainstay assumption in the previous review on cation transfer[1] and that the present review is designed to be compatible with the former one. It was there stated that the expected accuracy of the recommended data based on this assumption was ±3 kJ mol^{-1}, and this should apply also to the present review, although $\pm 3x_S$ kJ mol^{-1} should be a fairer estimate. Water−methanol mixtures are notable in that TPTB data are also available in three independent studies,[27−29] showing that $\Delta_t G°(Ph_4P^+) \approx \Delta_t G°(Ph_4As^+)$ within 0.7 kJ mol^{-1} over the entire composition range. This provides some indirect support for the use of the reference electrolyte approach. Accordingly, this approach, employing TATB, has been adopted in this review wherever possible.

2.3. Format and Organization of the Data

The Gibbs energies of transfer, $\Delta_t G°$(anion), data tables in the present review have the same format as those in the review on cation transfer.[1] This format includes the units, kJ mol^{-1}, and the molar concentration scale (mol dm^{-1}). The quantities reported in the literature have therefore been recalculated where necessary in order to conform to this choice. The preferred use of the molarity scale arises from the fact that it is the number density, ρ, of the solute particles that is required by statistical thermodynamics for the interpretation of the solvation energies of solutes.[30] If SI units are used for the number density, then $(\rho/\mathrm{m}^{-3}) = 1000N_A(c/\mathrm{mol\ dm}^{-3})$. The conversion of $\Delta_t G°$ of an ion from the molality scale is made according to

$$\Delta_t G°_{(c)} = \Delta_t G°_{(m)} + 2.303RT \log[d(W+S)/d(W)] \quad (5)$$

where d is the density of the indicated solvent mixture at the temperature where the transfer energetics are measured. Conversion from the mole fraction scale is according to

$$\Delta_t G°_{(c)} = \Delta_t G°_{(x)} + 2.303RT \log[M(W)d(W+S)/M(W+S)d(W)] \quad (6)$$

where M is the molar mass.

A common scale to express the composition of the mixed aqueous−organic solvent is also required, as the data in the literature are variously expressed on the mole fraction, mass fraction, and volume fraction scales. As used in the previous review on cations,[1] the mole fraction (percentage, $100x_{W+S}$) scale is employed here. This scale appears to best express the ability of the ions to sort the solvent molecules around them.[15,31] The density data required for conversions from volume-based scales were obtained by assuming a linear dependence of the density of the mixture on the solvent (mole fraction) composition, with the errors introduced thereby being <0.5 kJ mol^{-1}.

The original $\Delta_t G°$ data in the literature were thus converted to the molarity scale where necessary and interpolated numerically (by means of third or fourth power polynomials) to evenly spaced values of $100x_{W+S}$ for the purpose of tabulation. Lengthy interpolations are indicated by placing values in parentheses. Those $\Delta_t G°$(anion) data that were reported in the literature using the TATB assumption were tabulated directly, as shown in the “method” column in the tables. Those reported using other assumptions were dealt with as follows. If electrolyte data (in addition to or instead of anion transfer data) were reported, these were used directly; otherwise, reported anion and cation transfer data were combined to produce electrolyte data. These were then split back to anion transfer data by means of appropriate "selected" cation data from the previous review,[1] in order to make these two reviews compatible. The selected values, preferably those marked as **R** (recommended), but, if not available, then those marked **T** (tentative), generally pertain to H^+ or K^+ cations, but in some cases, the average of using several alkali metal cations produces converging values within 1 kJ mol^{-1}. The cation(s) from ref 1 used for this purpose is (are) recorded in the method column in the tables. The reliability of the data is commented upon in the texts that accompany the tables.

The Gibbs energies of transfer of "simple" inorganic anions from water to the most commonly used and representative aquo-organic solvent mixtures, over as complete a range of solvent compositions as possible, were gleaned from the literature, compiled and recalculated, where required. The resulting $\Delta_t G^\circ_{(c)}(A^{n-}, W \rightarrow W + S)$/kJ mol^{-1} values on the molarity scale at 298.15 K according to the TATB assumption are thus reported in Tables 1−19 (one for each cosolvent S) below. The order of the cosolvents is the same (when applicable) as used previously:[1] alkanols, ethers, carbonyl compounds, acetonitrile, amides, and dimethyl sulfoxide. The order of the anions in each table is OH^-, then the halides and pseudohalides, univalent oxyanions, the few organic anions included, and then multivalent anions. Very few data on the latter are available, since they strongly prefer the aqueous environment and transfer reluctantly (i.e., with large positive $\Delta_t G^\circ$) into aqueous organic solvents unless very rich in water.

In the tables, the values at each (rounded) solvent composition were averaged for those anions where mutually well agreeing results are available from at least two independent reliable studies, giving equal weight to each reported value. The averaged values shown in **bold** type have been classified in the reference column as recommended (***R***) when estimated to be accurate, within the constraints of the TATB assumption, to about $3x_S$ kJ mol^{-1}. Results from the average of two or more sets of data differing by more than 3 kJ mol^{-1} are designated as tentative (***T***), with a likely accuracy of $\sim 5x_S$ kJ mol^{-1}. Values in { } are probably reliable but are due to a single source only. Rejected data are identified by enclosure in square brackets [ ], and the reason(s) for rejection is (are) stated in the text. Such data are not used in the calculation of averaged values. As mentioned above, values in ( ) denote those obtained from lengthy interpolations. In the cases of anion transfer into aqueous alkanols, the selections of recommended values in the previous review by the author[14] were adhered to (but the solvent scale is changed to the mole fraction one, requiring recalculation to the evenly spaced mole percentages). Hence, the data for such anions where recommendations could be made[14] are summarized by just one row and readers interested in values published prior to 1989 should consult this reference. More recent data, however, are shown in the present tables, but they do not alter significantly the prior recommendations.

3. Anion Transfer Gibbs Energies from Water to Mixed Aqueous Solvents

3.1. Transfer to Aqueous Methanol

The transfer Gibbs energies of anions into water + methanol (MeOH) mixtures are the most extensively studied of all transfer values into aqueous/organic solvent mixtures. Values of $\Delta_t G^\circ(A^{n-}, W \rightarrow W + MeOH)$ for a wide variety of monovalent anions over the entire solvent composition range and for some divalent anions for water-rich mixtures are given in Table 1. The many earlier $\Delta_t G^\circ$ values for chloride, bromide, iodide, perchlorate, picrate, and tetraphenylborate for these mixtures listed by Marcus[14] have not been repeated here, with only the final recommended values being reported. For other anions, results based on the TATB method are reported directly; those that were not so based were recalculated using salt and recommended cation values. The numerous independent studies of the potassium ion, leading to well consistent recommended values,[1] permitted the $\Delta_t G^\circ$ of this cation together with $\Delta_t G^\circ$ data for potassium salts to be used for obtaining the $\Delta_t G^\circ$ of the anions of these salts. In some cases, noted in Table 1, other cations with recommended values have been employed for this purpose.

Poor agreement exists between the values shown for OH^-. The decreasing trend of $\Delta_t G^\circ$ with increasing x_{MeOH} derived from the data by Pavelek and Mollin[32] is unreasonable. This trend is due to the value of

$$\Delta_t G^\circ(H^+) + \Delta_t G^\circ(OH^-) = RT\{\ln[pK_{W+MeOH} - pK_W] + \ln(1 + Q)\} \quad (7)$$

derived from their tabulated data[32] where Q is the ratio of the lyate ion concentrations. It is not due to erroneous $\Delta_t G^\circ(H^+)$, since for other anions its use with acids leads to results consistent with those for salts. On the other hand, the values for F^-, CN^-, and SCN^- that could not be sufficiently well evaluated previously[14] have by now been augmented by additional data, and recommended sets are presented. The results for several oxyanions, unfortunately, extend only over water-rich compositions. The $\Delta_t G^\circ$ values of most anions, except for the hydrophobic anions Pic^- and BPh_4^-, are positive (though some are near zero or slightly negative for water-rich mixtures) and increase with the methanol content. If data were available for divalent anions for methanol-rich mixtures, they would show much higher positive values than those for the univalent anions, and in this respect the data for $Cr_2O_7^{2-}$,[33] even in water-rich mixtures, appear to be incorrect. One reason why the data for divalent anions do not extend to higher methanol contents is the diminishing permittivity of such solvent mixtures, leading to ion pairing even at low salt concentrations and, hence, to the inability of determining the ionic Gibbs energy of transfer. That the data for $Fe(CN)_6^{3-}$ extend over the entire composition range means that these data need to be considered with caution, since corrections for activity coefficients and ion association were knowingly neglected by Abraham et al.[28]

The small negative values of $\Delta_t G^\circ$ in water-rich mixtures with methanol for some anions, mentioned above, are a real phenomenon. Such mixtures can provide hydrogen bonds more readily than pure water, since $CH_3O(H_2O)_n^-$ is a weaker base than $HO(H_2O)_m^-$.[1] Why this does not apply to the lighter halide anions or the halate ones but does to, e.g., hydroxide, cyanide, and perchlorate is not readily apparent. The trends in $\Delta_t G^\circ(A^-)$ for various anions are discussed in section 4.

Table 1. Standard Molar Gibbs Energies of Transfer of Anions from Water to Methanol (MeOH) + Water Mixtures at 298.15 K, $\Delta_t G°$(ion)/kJ mol^{-1}, Molarity Scale

	$\Delta_t G°$(ion)/kJ mol^{-1} at the following values of 100x_{MeOH}												
	5	10	20	30	40	50	60	70	80	90	100	method	ref
OH^-	−0.2	−0.3	−0.1	0.6	1.8	3.4	5.3	7.4	9.4	11.2	12.4	TPTB	28
	−0.1	−0.2	−0.1	0.4	1.6							TATB	33
	[3.6]	[2.2]	[1.0]	[1.0]	[1.5]	[1.6]	[2.5]	[2.2]	[1.9]			H^+	32
F^-	0.6	1.4	3.0	4.9	6.8	8.8	10.7	12.6	14.2	15.7	16.7	TATB	*a*
	0.7	1.6	3.4	5.2	6.9	8.8	10.8	12.9	15.3	17.8	20.7	TATB	28
	0.8	1.6	3.1	4.7	6.3	8.0	9.7	11.6	13.7	15.9	18.3	TATB	*b*
		[0.1]	[0.9]	[2.2]	[3.7]	[5.4]	[7.9]	9.9	12.7	15.7	20.1	K^+	*c*
	0.6	1.3	3.1	5.3	7.3	9.5	11.4	13.1	14.6	16.1	17.8	Na^+	*d*
		1.5	3.2	5.0	6.3	8.5	10.0	11.2	14.0	16.5	19.5	Li^+, Na^+	*e*
	0.7	**1.5**	**3.2**	**5.1**	**6.7**	**8.7**	**10.5**	**12.2**	**14.5**	**16.4**	**20.1**		**R**
Cl^-	**0.2**	**0.6**	**1.6**	**2.8**	**4.1**	**5.5**	**7.0**	**8.6**	**10.2**	**11.7**	**13.2**	**TATB**	**R 14**
Br^-	**0.0**	**0.1**	**0.8**	**1.7**	**2.8**	**4.1**	**5.4**	**6.9**	**8.4**	**9.8**	**11.1**	**TATB**	**R 14**
I^-	**−0.2**	**−0.3**	**−0.1**	**0.3**	**0.9**	**1.7**	**2.6**	**3.7**	**4.9**	**6.1**	**7.3**	**TATB**	**R 14**
CN^-	−0.9	−1.5	−2.0	−2.4								K^+	*f*
	−0.8	−1.5	−2.0	−1.7	−0.8	0.5	2.1	3.4	5.6	7.7	10.4	K^+	*g*
	−1.0	−1.6	−2.3	−2.4	−1.9	−0.9	0.5	2.2	4.2	6.3	8.6	TATB	28
	−0.9	**−1.5**	**−2.1**	**−2.2**	**−1.4**	**−0.2**	**1.3**	**2.8**	**4.9**	**7.0**	**9.5**	**TATB**	**T**
N_3^-	2.1	(3.5)	(5.9)	.8	9.3	10.5	11.3	(12.1)	13.0	14.3	16.4	K^+	*h*
SCN^-	0.4	0.6	1.1	1.2							4.4	Ag^+	*i*
	0.0	0.0	−0.4	−2.2								H^+	*j*
	−0.4	−0.7	−1.0	−1.1							5.6	TATB	28
	−0.5	−0.8	−1.0	−0.5	0.3	1.4	2.8	4.1				TATB	*k*
	−0.4	−0.7	−0.9	−0.6	0.2		3.0					TATB	33
	0.0	0.0	−0.7	−1.1	−1.3	−1.4	−0.5	0.5	2.8	3.8	4.6	H^+	*l*
	−0.2	**−0.4**	**−0.8**	**−1.2**	**−0.5**	**0.0**	**1.8**	**2.3**	{**2.8**}	{**3.8**}	{**4.6**}	**TATB**	**T**
NO_3^-	−0.1	0.0	0.6	1.5	2.4							TATB	33
	−0.2	−0.1	0.4	1.4	2.5							TPTB	*m*
ClO_3^-		1.1	2.2	3.0								K^+	*n*
BrO_3^-	0.9	1.8	3.2	4.2	4.9							TATB	*k*
	0.7	1.4	3.0	4.2								TATB	33
		1.9	3.6	5.1								K^+	*n*
IO_3^-	1.0	2.1	4.4	6.7	9.2							TATB	*k*
	1.0	2.0	4.1	6.6								TATB	33
		3.1	6.1	8.7								K^+	*n*
ClO_4^-	−0.1	−0.2	−0.2	0.0	0.5	1.1	1.9	2.9	4.1	5.5	7.1	TATB	*o*
	−0.3	−0.3	−0.2	0.1	0.5	1.1	1.8	2.6	3.6	4.7	5.9	TATB	28
	0.0	−0.1	−0.1	0.0	0.3	0.9	1.6	2.5	3.6	4.9	6.4	TATB	*k*
	0.2	0.1	−0.1	0.0	0.3							TPTB	*m*
	0.0	0.2	0.2	−0.3								K^+	*n*
	−0.1	**−0.2**	**−0.2**	**0.0**	**0.4**	**1.0**	**1.8**	**2.7**	**3.8**	**5.0**	**6.5**	**TATB**	**R**
ReO_4^-	−0.3	−0.7	−1.3	−1.9								TATB	28
IO_4^-		0.4	0.6	0.3								K^+	*n*
BF_6^-	−0.8	−1.3	−1.5	−1.1	−0.5		0.6				3.1	TATB	*p*
PF_6^-	0.6	0.6	−0.4	−1.1	−0.9		−0.7					TATB	*p*
$HC_2O_4^-$	0.8	1.1	2.0	3.3	4.8	6.2	7.9	9.0	10.7			H^+, K^+	*q*
$PhCO_2^-$	1.0	1.9	4.0	6.4	9.0	11.1	13.3					H^+	*r*
Pic^-	**−0.3**	**−0.8**	**−1.8**	**−2.7**	**−3.4**	**−3.9**	**−4.1**	**−4.1**	**−4.0**	**−3.7**	**−3.6**	**TATB**	**R 14**
		0.0	−0.9	−2.7								K^+	*n*
BPh_4^-	**−2.0**	**−4.2**	**−8.2**	**−11.6**	**−14.6**	**−17.0**	**−19.0**	**−20.5**	**−21.6**	**−22.3**	**−22.7**	**TATB**	**R 14**
		−3.8	−7.8	−12.2								K^+	*n*
	−2.3	−4.5	−9.0	−13.2	−16.8	−19.7	−21.4					TATB	36
$C_2O_4^{2-}$	2.9	4.6	8.2	11.3	16.4	20.0	23.9	26.2	29.2			H^+, K^+	*q*
SO_4^{2-}	3.3	6.3	11.7	16.0								K^+	*f*
CrO_4^{2-}	1.1	2.3	5.0									TATB	33
$Cr_2O_7^{2-}$	[−0.2]	[−0.2]	[0.1]	[0.7]	[1.3]							TATB	33
$S_2O_6^{2-}$	1.3	3.1	7.4	12.4	17.5							TPTB	*m*
$S_2O_8^{2-}$	0.4	1.1	3.5	6.7								K^+	*f*
$Fe(CN)_6^{3-}$	−2.0	−2.7	−2.9	−1.7	0.9	4.9	10.2	16.8	24.7	33.9	44.2	TATB	28

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3.2. Transfer to Aqueous Ethanol

The transfer Gibbs energies of anions into water + ethanol (EtOH) mixtures have also been extensively studied. Values of $\Delta_t G°(A^{n-},W \rightarrow W+EtOH)$ for a variety of monovalent anions over most of the solvent composition range and for some divalent anions for water-rich mixtures are given in Table 2. For these aqueous−organic mixtures, recommended $\Delta_t G°$ values from ref 1 for H^+, K^+, and Ag^+ have been used with acid and salt transfer data to obtain the anion values where no direct use of the TATB method was reported. It

Table 2. Standard Molar Gibbs Energies of Transfer of Anions from Water to Ethanol (EtOH) + Water Mixtures at 298.15 K, $\Delta_t G°$(ion)/kJ mol^{-1}, Molarity Scale

	$\Delta_t G°$(ion)/kJ mol^{-1} at the following values of 100x_{EtOH}												
	5	10	20	30	40	50	60	70	80	90	100	method	ref
OH^-		1.7	4.4	7.4	8.2							H^+	*a*
	0.9	2.1	5.4	9.2								TATB	*b*
	[9.1]	[6.7]	[5.2]	[5.9]	[5.5]	[5.3]	[4.3]	[3.1]	[0.9]			H^+	32
F^-	0.9	2.6	7.2	11.5	14.7	16.6	17.7	18.7	20.3	22.7	25.8	TATB	*c*
	1.4	2.6	7.1	11.4	14.8	17.2	19.3					Na^+	*d*
	1.4	2.6	7.5	12.0	14.5	17.0	18.0	19.5	20.0	22.0	27.0	Li^+, Na^+	*e*
	1.2	**2.6**	**7.3**	**11.6**	**14.7**	**16.9**	**18.3**	**{19.1}**	**{20.2}**	**{22.4}**	**{26.4}**		**T**
Cl^-	0.7	2.2	4.9	7.2	9.2	11.0	12.6	14.2	15.7	(17.4)	19.3	TATB	*b*
	0.6	1.2	2.7	5.1								TATB	*f*
	0.6	**1.7**	**4.5**	**7.5**	**10.1**	**12.2**	**13.6**	**(14.7)**	**15.7**	**(17.3)**	**20.3**	**TATB**	**R, 14**
	0.4	0.8	1.3	2.2	3.3	4.5	5.8	7.1	8.4	9.8		see text	20
Br^-	0.9	1.3	3.9	(6.8)	7.7	8.7	(9.1)	9.5	9.1	(6.5)	1.0	H^+	*g*
	(0.5)	1.1	2.5	4.0	5.6	7.5	9.5				19.0	*	*h*
	0.5	0.6	2.5	5.2	6.1	7.5	8.5	9.8	10.3	8.5	3.7	H^+	*i*, 60
	0.0	0.6	3.2	7.0								TATB	*b*
	0.0	0.3	1.3	3.3								TATB	*f*
	0.4	**0.7**	**2.7**	**5.6**	**6.9**	**8.1**	**8.8**	**9.7**	**{10.3}**		**{19.0}**[†]	**TATB**	**T**
I^-	(−0.1)	0.0	0.6	1.6	3.1	4.7	6.6				14.0	*	60
	−0.6	−0.6	1.1	4.4								TATB	*b*
	−0.3	−0.4	0.1	1.0	1.8	2.0						TATB	*f*
	−0.3	**−0.3**	**0.6**	**2.3**	**{2.8}**	**3.4**					**{14.0}**[†]	**TATB**	**T**
CN^-	0.0	0.2	1.5	2.5	3.6	4.4	5.1	6.6				K^+	*j*
	2.8	4.2	5.8	6.3	6.8	7.8	9.1	9.8	8.3			Ag^+	9
	−0.2	0.0	0.5	1.2	2.2	3.7	5.7					TATB	*b*
SCN^-	−0.4	−0.7	−0.3	0.8	2.3	3.7	(4.8)	(4.9)	3.9	(1.1)	−3.6	H^+	*k*
NO_3^-	1.1	2.3	4.7	7.0	9.1							TATB	*b*
ClO_4^-	1.5	2.6	4.8	5.8	6.2	6.1					9.3	K^+	*l*
	0.2	0.7	1.6	2.4	3.1	3.9	4.7	5.6	6.7	(8.1)	9.8	TATB	*b*
$Ag(CN)_2^-$	2.4	3.4	4.3	4.2	4.5	5.5	6.8	7.6	6.1			Ag^+	9
	−0.8	−1.3	−1.7	−1.2	−0.3	0.9	2.1	3.2	3.8			TATB	*b*
$Au(CN)_2^-$	1.5	1.4	0.3	−0.9	−0.7	1.4	4.7	7.5	7.4			Ag^+	9
	−2.0	−3.5	−5.2	−5.5	−4.8	−3.4	−1.6	0.1	1.5			TATB	*b*
$HC_2O_4^-$	1.0	2.3	5.5	9.2	10.9	12.6	13.3	13.3				K^+	*m*
$CH_3CO_2^-$	−1.1	−1.4	−2.3	−3.2	−4.2	−5.1	−5.9	−6.5	−6.9	(−6.9)	−6.6	TATB	*b*
$PhCO_2^-$	1.6	3.3	7.7	12.1	14.1	15.5	15.7	15.3				H^+	*n*
Pic^-	−0.5	−1.0	−1.4	−1.4	−1.3	−1.1	−1.0	−1.1	−1.2	−1.2	−0.6	TATB	*l*
	0.8	1.0	0.3	−0.6	−1.1	−1.2	−1.1	−0.9	−0.9	−0.9	−0.3	*	*o*
	−0.4	−1.0	−2.3	−3.1	−3.3	−3.0	−2.5	−1.9	−1.3	−0.6	0.5	TATB	*p*
	−0.6	−1.3	−2.3	−2.8	−3.0	−2.8	−2.5	−1.9	−1.4	(−0.8)	−0.3	TATB	*b*
	−0.7	−1.6	−3.4	−5.0	−5.9	−5.9						TATB	*f*
	−0.3	**−0.8**	**−1.8**	**−2.8**	**−2.9**	**−2.8**	**−1.8**	**−1.5**	**−1.2**	**−0.9**	**−0.2**		**T**
BPh_4^-	−3.4	−6.9	−12.5	−16.7	−19.5	−21.2	−22.0	−21.9	−21.3	−20.2	−18.9	TATB	*l*
	−2.4	−5.4	−10.4	−14.1	−16.8	−18.6	−19.7	−20.3	−20.6	−20.8	−21.0	*	*n*
	−3.6	−7.1	−12.7	−16.5	−18.8	−20.0	−20.3	−20.2	−19.9	−19.9	−20.3	TATB	*o*
	−4.0	−7.7	−13.2	−16.8	−18.7	−19.4	−19.3	−18.8	−18.2	−18.1	−18.7	**	*h*
	−3.6	−7.8	−13.0	−16.9	−19.2	−20.3	−20.6	−20.5	−20.3	(−20.3)	−20.9	TATB	*b*
		−10.5	−16.1	−19.0	−20.2	−20.7	−21.0	−21.6	−22.1	−22.4	−21.7	TATB	*p*
	−3.3	−6.6	−12.5	−17.2	−20.1	−20.9						TATB	*f*
	−3.6	**−7.3**	**−12.9**	**−16.5**	**−18.6**	**−19.8**	**−20.2**	**−20.3**	**−20.4**	**−20.6**	**−21.3**	**TATB**	**R, 14**
$C_2O_4^{2-}$	3.4	7.3	15.3	23.7	27.6	31.1	32.6	33.5				H^+	*m*
SO_4^{2-}	5.5	10.3	19.9									TATB	*b*
CrO_4^{2-}	2.5	4.4	6.9	8.6	10.7							TATB	*b*
	2.0	5.1	13.0	20.9	26.5	27.1						H^+	*k*
$S_2O_3^{2-}$	2.8	5.2	10.9									TATB	*b*
$S_2O_6^{2-}$	2.1	5.1	12.0									TATB	*b*
	2.1	5.6	14.9	23.3	26.5							TATB	*q*
SiF_6^{2-}	4.5	8.7	13.7									TATB	*b*

*Based on the assumption that $\Delta_t G°(i\text{-}Pe_3BuN^+) = \Delta_t G°(BPh_4^-)$. **Based on an extrapolation of MX data to an infinite radius of M^+. [†] Adopted from Marcus.[12] [a] Gillet, H.; Avedikian, L.; Morel, J.-P. *Can. J. Chem.* **1975**, *53*, 455. [b] Blandamer, M. J.; Briggs, B.; Burgess, J.; Elvidge, D.; Guardado, P.; Hakin, A. W.; Radulovich, S.; Hubbard, C. D. *J. Chem. Soc., Faraday Trans. 1* **1988**, *84*, 2703. [c] Hefter, G. T.; McLay, P. J. *J. Solution Chem.* **1988**, *17*, 535. [d] Hernandez-Luis, F.; Vazquez, M. V.; Esteso, M. A. *J. Mol. Liq.* **2003**, *108*, 283. [e] Senanayake, G.; Hefter, G. *Monatsh. Chem.* **2003**, *134*, 669. [f] Sinha, R.; Kundu, K. K. *Indian J. Chem. A* **1997**, *36A*, 541. [g] Schwabe, K.; Urlass, R.; Ferse, A. *Ber. Bunsen-Ges. Phys. Chem.* **1964**, *68*, 46. [h] Bax, D.; DeLigny, C. L.; Remijnse, A. G. *Recl. Trav. Chim.* **1972**, *91*, 965. [i] Elsemongy, M. M.; Fouda, A. S. *Electrochim. Acta* **1981**, *26*, 1125. [j] Blandamer, M. J.; Burgess, J.; Duffield, A. J. *J. Chem. Soc., Dalton Trans.* **1980**, 1. [k] Tsurko, E. N.; Rubtsov, V. I.; Alexandrov, V. V. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 1345. [l] DeLigny. C. L.; Bax, D.; Alfenaar, M.; Elferink, M. G. L. *Recl. Trav. Chim.* **1969**, *88*, 1183. [m] Gumtya, V. S. K.; Lahiri, S. C.; Aditya, S. *Z. Phys. Chem.* **2002**, *216*, 971. [n] Popovych, O.; Dill, A. J. *Anal. Chem.* **1969**, *41*, 456. [o] Popovych, O.; Gibovsky, A.; Berne, D. H. *Anal. Chem.* **1972**, *44*, 811. [p] Gomaa, E. A. *Thermochim. Acta* **1989**, *156*, 91. [q] Abdur-Rashid, K.; Dasgupta, T. P.; Burgess, J. *Transition Met. Chem.* **2005**, *30*, 948.

was possible to derive average values from those derived from independent reports by several authors for some anions: Cl^-, Br^-, I^-, Pic^-, and BPh_4^-. Note that the selected (tentative) values for transfer from water into neat ethanol for Br^- and I^- are from the review by Marcus,[12] because the values for the ethanol-rich aqueous mixtures cannot be reliably extrapolated to $x_{EtOH} = 1$.

The comment above concerning the OH^- values in aqueous methanol from Pavelek and Mollin[32] applies to the values in aqueous ethanol too, but for mixtures with $x_{EtOH} \geq 0.2$ they may be more nearly correct. The discrepancies noted between the two sets of data for the complex cyanides, $Ag(CN)_2^-$ and $Au(CN)_2^-$, may be due to the value of $\Delta_t G°(Ag^+)$ employed with the salt data of Muir et al.,[9] that in

Table 3. Standard Molar Gibbs Energies of Transfer of Anions from Water to 2-Propanol (iPrOH) + Water Mixtures at 298.15 K, $\Delta_t G°$(ion)/kJ mol^{-1}, Molarity Scale

	$\Delta_t G°$(ion)/kJ mol^{-1} at the following values of $100x_{i-\mathrm{PrOH}}$								
	2	5	10	15	20	25	40	method	ref
OH^-		[9.1]	[7.5]		[6.5]		[5.9]	H^+	32
Cl^-	1.4	2.9	5.1	6.8	8.1	8.9		H^+	*a*, *b*
	0.9	2.2	4.0	5.7	7.1	8.4		H^+	37
	0.6	1.6	2.9	4.2	5.4	6.3		H^+	*c*
	1.2	2.7	4.8	6.6	8.0	8.9		H^+	*d*, 60
	0.7	1.5	2.9	5.1	6.3	7.2		H^+	*d*
	0.8	2.0	3.7	5.1	6.3	7.2		TATB	*e*
		0.4	1.2		1.2		2.2	see text	20
	1.0	**2.2**	**3.9**	**5.5**	**6.9**	**8.0**		**TATB**	**R**
Br^-	0.6	1.5	2.7	3.8	4.9	5.7		H^+	*f*
	0.6	1.4	2.7	3.7	4.6	5.4		TATB	*e*
	0.6	**1.5**	**2.7**	**3.8**	**4.8**	**5.6**		**TATB**	**T**
I^-	[1.3]	[2.6]	[3.9]	[5.2]	[6.3]			H^+	35
	0.4	0.8	1.4	2.0	2.6	3.1	4.2	TATB	*e*
ClO_3^-	1.3	2.9	4.8	5.7				K^+	*g*
BrO_3^-	1.4	3.45	5.9	7.3				K^+	*g*
IO_3^-	2.3	5.1	8.7	10.8				K^+	*g*
ClO_4^-	0.8	1.7	2.7	3.4				K^+	*g*
IO_4^-	0.7	1.3	1.8	1.6				K^+	*g*
$PhCO_2^-$	0.1	1.5	3.8	6.1	6.7			H^+	*h*
Pic^-	0.6	0.4	−1.4	−3.4	−3.6	0.1		TATB	*d*
	0.4	0.6	−0.1	−2.0				K^+	*g*
	−0.1	−0.9	−2.2	−3.3	−4.2	−4.9	−6.1	TATB	*e*
BPh_4^-	−1.8	−5.2	−11.2	−16.0	−17.7	−14.4		TATB	*d*
	−0.9	−2.6	−7.4	−14.6				K^+	*g*
	−2.5	−6.2	−11.0	−14.6	−17.1	−18.7	−21.0	TATB	*e*
$S_2O_6^{2-}$	2.0	5.3	10.5	15.5	20.2	24.6		TATB	*i*

[a] Roy, R. N.; Bothwell, A. *J. Chem. Eng. Data* **1970**, *15*, 548. [b] Roy, R. N.; Vernon, W.; Bothwell, A. L. M. *J. Chem. Thermodyn.* **1971**, *3*, 769. [c] Elsemongy, M. M.; Fouda, A. S. *J. Electroanal. Chem.* **1980**, *114*, 25. [d] Basu Mulick, I. N.; Kundu, K. K. *Indian J. Chem. A* **1984**, *A23*, 812. [e] Sinha, R.; Kundu, K. K. *Indian J. Chem. A* **1997**, *36A*, 541. [f] Schwabe, K.; Müller, R. *Ber. Bunsen-Ges. Phys. Chem.* **1970**, *74*, 1248. [g] Benko, J.; Vollarova, O.; Cernusak, I.; Pappova, A. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 4935. [h] Bhattacharya, A. K.; Pal, A.; Lahiri, S. C. *J. Indian Chem. Soc.* **1985**, *62*, 953. [i] Abdur-Rashid, K.; Dasgupta, T. P; Burgess, J. *Transition Met. Chem.* **2005**, *30*, 948.

turn is marked as tentative (***T***),[1] being reported from one source only, Kim and Duschner.[34] This applies also to the values of $\Delta_t G°(CN^-)$.

Divalent anions show relatively large Gibbs energies of transfer even in water-rich mixtures, as expected from the hydrophilicities of the anions and the moderate ability of ethanol to provide hydrogen bonds, especially in the presence of water. Positive values of $\Delta_t G°$ are noted also for the smaller monovalent anions, although the larger, less hydrophilic, ones have negative values. The inability to obtain reliable $\Delta_t G°$ values for the divalent anions as the content of the cosolvent increases has already been commented on above, when dealing with aqueous methanol.

3.3. Transfer to Aqueous 2-Propanol

The transfer Gibbs energies of anions into water + 2-propanol (*i*-PrOH) mixtures have not been extensively studied. Values of $\Delta_t G°(A^{n-}, W \rightarrow W + i\text{-PrOH})$ for some univalent anions for only water-rich compositions and for one divalent anion are given in Table 3. The comment given above concerning nonvalidity of the OH^- data[32] is appropriate here too. The data for Cl^- and Br^- could be averaged, and recommended sets (respectively tentative) are provided. However, the transfer data for HI by Das et al.,[35] and, hence, the derived values of I^-, appear to be incorrect, because they lead to much too high $\Delta_t G°(I^-)$ values compared to those of $\Delta_t G°(Br^-)$, whereas those values from Sinha and Kundu[36] appear to be reasonable.

Table 4. Standard Molar Gibbs Energies of Transfer of Anions from Water to 2-Methyl-2-propanol (*t*-BuOH) + Water Mixtures at 298.15 K, $\Delta_t G°$(ion)/kJ mol^{-1}, Molarity Scale

	$\Delta_t G°$(ion)/kJ mol^{-1} at the following values of $100x_{t-\mathrm{BuOH}}$								
	2	5	10	15	20	30	40	method	ref
OH^-		2.4	5.2	(6.5)	7.7			H^+	*a*
	1.6	4.5	9.3					TATB	*b*
F^-	1.0	3.2	6.5	9.6				TATB	*c*
	0.9	2.7	5.7	8.6	11.6	17.4	23.2[a]	Li^+, Na^+	72
	1.0	**3.0**	**6.1**	**9.1**	{**11.6**}	{**17.4**}	{**23.2**}	**TATB**	**T**
Cl^-	0.5	2.1	4.8	7.6				TATB	*d*
	1.5	4.2	6.9	8.3	10.3			H^+	*e*
	1.3	4.1	7.1	8.1	8.7			H^+	*f*
	1.0	2.7	5.3	7.9				TATB	*g*
	1.3	3.0	6.5	9.7	11.6	(18.0)		M^+ *	*h*
	1.1	2.8	5.0	6.6	7.5			TATB	*k*
	0.4	2.3	4.9	6.4	7.6			H^+	*i*
	1.0	**3.0**	**5.8**	**7.8**	**9.1**			**TATB**	**R**
Bt^-	0.9	3.0	5.4	6.8	9.2			H^+	*e*
	0.6	2.7	5.7	7.5	9.5			H^+	*e*
	0.4	2.2	5.0	6.7	8.6			H^+	*j*
	0.3	1.6	4.0	6.7				TATB	*b*
	0.6	1.7	3.5	5.1	6.5			TATB	*k*
	0.6	**2.2**	**4.7**	**6.6**	**8.5**			**TATB**	**R**
I^-	0.4	2.0	4.1	5.2	7.0			H^+	*e*
	0.0	0.9	2.7	5.0				TATB	*b*
	0.1	0.8	2.0	3.2	4.4			TATB	*k*
	0.2	**1.2**	**2.9**	**4.5**	{**5.7**}			**TATB**	**T**
ClO_3^-	0.2	1.9	5.1					K^+	*l*
BrO_3^-	0.5	2.6	6.3					K^+	*l*
IO_3^-	1.3	4.2	8.7					K^+	*l*
ClO_4^-	−0.2	0.8	2.3					K^+	*l*
	0.4	1.2	2.3	3.0	3.6	4.3	5.1 **	TATB	*m*
IO_4^-	−0.2	0.3	1.9					K^+	*l*
Pic^-	−0.7	−1.6	−2.8	−3.5				TATB	*b*
	0.6	0.2	−2.4	−4.2	−1.7			TATB	*g*
	0.4	−0.2	−2.6	−4.5	−3.2			TATB	*k*
	{**0.1**}	**−0.5**	**−2.6**	**−4.1**	**−2.5**			**TATB**	**T**
BPh_4^-	−2.9	−7.4	−13.1	−16.2				TATB	*b*
	−3.0	−7.8	−14.6	−18.0	−15.8			TATB	*g*
	−3.6	−8.7	−14.5					R_4N^+	*n*
	−2.8	−8.5	−15.2	−15.7	−17.6			TATB	*k*
	−3.1	−6.8	−11.4	−14.3	−15.8	−15.7	−13.6 **	TATB	*m*
	−3.1	**−7.8**	**−13.8**	**−16.1**	**−16.4**			**TATB**	**T**
$S_2O_6^{2-}$	1.3	1.9	11.3	16.9	20.0			TATB	*m*

* Average of using Li^+, Na^+, K^+, Rb^+, and Cs^+ data from ref 1. **Also data for $x_{t-\mathrm{BuOH}} = 0.5$: $\Delta_t G°$(ion)/kJ mol^{-1} = 6.4 and −12.0, and $x_{t-\mathrm{BuOH}} = 0.6$: $\Delta_t G°$(ion)/kJ mol^{-1} = 8.9 and −13.1, for ClO_4^- and BPh_4^-, respectively. [a] Gillet, H.; Avedikian, L.; Morel, J.-P. *Can. J. Chem.* **1975**, *53*, 455. [b] Juillard, J.; Tissier, T. *Electrochim. Acta* **1982**, *27*, 123 [c] Juillard, J.; Tissier, T.; Barczynska, J.; Mokrzan, J.; Taniewska-Osinska, S. *J. Chem. Soc., Faraday Trans. 1* **1985**, *81*, 3081. [d] Pointud, Y.; Juillard, J.; Morel, J. P.; Avedikian, L. *Electrochim. Acta* **1974**, *19*, 229. [e] Bose, K.; Das, A. K.; Kundu, K. K. *J. Chem. Soc., Faraday Trans. 1* **1975**, *71*, 1838. [f] Khoo, K. H.; Chan, C.-Y. *Aust. J. Chem.* **1975**, *28*, 721. [g] Basu Mulick, I. N.; Kundu, K. K. *Indian J. Chem. A* **1984**, *A23*, 812. [h] Elsemongy, M. M.; Abdel-Khalek, A. A. *Thermochim. Acta* **1990**, *158*, 107. [i] Elsemongy, M. M. *Electrochim. Acta* **1978**, *23*, 957. [j] Elsemongy, M. M. *J. Electroanal. Chem.* **1978**, *90*, 77. [k] Sinha, R.; Kundu, K. K. *Indian J. Chem. A* **1997**, *36A*, 541. [l] Benko, J.; Vollarova, O. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 855. [m] Abdur-Rashid, K.; Dasgupta, T. P.; Blundell, N. J.; Burgess, J.; Drasdo, D. N. *Transition Met. Chem.* **2005**, *30*, 176. [n] Talukdar, H.; Kundu, K. K. *J. Phys. Chem.* **1992**, *96*, 970.

It should be noted that hardly any data exist for transfer of anions into aqueous 1-propanol[14] and that no corresponding values for cation transfer into aqueous 1-propanol could be evaluated.[1] Hence, the published data for the $\Delta_t G°$ values of HCl and RbCl from Smits et al.[37] could not be split into the ionic values.

3.4. Transfer to Aqueous 2-Methyl-2-propanol

The transfer Gibbs energies of anions into water-rich aqueous 2-methyl-2-propanol (*t*-BuOH) mixtures have been studied somewhat more extensively than those for aqueous 2-propanol. Values of $\Delta_t G°(A^{n-}, W \rightarrow W + t\text{-BuOH})$ for some monovalent anions and for one divalent anion are given in

Table 4. It should be recalled that, of the four butanols, only *tert*-butanol (2-methyl-2-propanol) is completely miscible with water, and therefore, the transfer of electrolytes into such mixtures could be studied. Nevertheless, for the reasons discussed above for aqueous methanol, the reported values are confined to the water-rich range of compositions where the permittivity is sufficiently large to permit ionic dissociation. There are sufficient consistent data from independent sources on the transfer of the halide anions to permit the listing of sets of recommended values for Cl^- and Br^- and at least tentative values for F^- and I^-. Tentative values could also be listed for Pic^- and BPh_4^- for the same reason.

Table 5. Standard Molar Gibbs Energies of Transfer of Anions from Water to 2-Methoxyethanol (MeOEtOH) + Water Mixtures at 298.15 K, $\Delta_tG°$(ion)/kJ mol^{-1}, Molarity Scale

	$\Delta_tG°$(ion)/kJ mol^{-1} at the following values of $100x_{MeOEtOH}$								
	2	5	10	15	20	30	40	method	ref
OH^-	1.1	2.8	5.2	7.3	8.9	11.1	11.6	TATB	68
F^-	0.9	2.5	4.9	7.0	8.7	11.3	12.7	TATB	68
Cl^-	0.7	2.0	4.0	5.9	7.6	10.4	12.4	TATB	39
	0.8	2.2	4.6	6.8	8.9	12.7	16.0	TATB	38
	0.9	2.1	4.1	6.1	7.8	10.7	12.1	K^+ *	*a*
	0.8	**2.1**	**4.2**	**6.3**	**8.1**	**11.3**	**13.5**	**TATB**	**T**
Bt^-	0.4	1.4	2.9	4.4	5.7	8.3	10.0	TATB	39
	0.4	1.6	3.5	5.4	7.1	10.4	13.4	TATB	38
	0.5	1.4	2.9	4.5	6.1	8.5	9.4	K^+ *	*a*
	0.4	**1.5**	**3.1**	**4.8**	**6.3**	**9.1**	**10.9**	**TATB**	**T**
I^-	0.2	0.6	1.3	1.9	2.6	3.8	5.0	TATB	39
	0.0	0.5	1.4	2.3	3.4	5.6	8.2	TATB	38
	0.3	0.7	1.4	2.1	2.8	4.1	4.9	K^+ *	*a*
	0.2	**0.6**	**1.4**	**2.1**	**2.9**	**4.5**	**6.0**	**TATB**	**T**
$PhCO_2^-$	0.3	1.0	2.0	3.0	3.9	5.4	6.7†	Cl^- **	*b*
Pic^-	0.1	0.2	0.1	−0.3	−0.6	−1.2	−2.0	TATB	39
BPh_4^-	−2.4	−4.8	−8.4	−11.6	−14.4	−18.8	−21.6	TATB	39

* K^+ values calculated from the TATB assumption and data from Bhattacharya et al.[39] **Cl^- values from Bhattacharya et al.[39] (as in this table) and HCl data from Smits et al.[37] to yield H^+ values, that with H^+ + $PhCO_2^-$ values from Gomaa's[b] data yield $PhCO_2^-$ values. † Also a value for $x_{2MeOEtOH} = 0.5$, $\Delta_tG°(PhCO_2^-)$/kJ mol^{-1} = 7.3. [a] Das, B. *Bull. Chem. Soc. Jpn* **1994**, *67*, 1217. [b] Gomaa, E. A. *Thermochim. Acta.* **1989**, *156*, 91.

3.5. Transfer to Aqueous 2-Methoxyethanol

The few data on the transfer Gibbs energies of anions into water-rich aqueous 2-methoxyethanol (MeOEtOH) mixtures, $\Delta_tG°(A^{n-},W\rightarrow W+MeOEtOH)$ are shown in Table 5. Still, there are independent data from three sources on each of Cl^-, Br^-, and I^- to permit averaging and listing of sets of tentative values. The values from Guha and Kundu[38] are systematically higher than those from the other two sources, but not excessively, so that they could be included in the averages. Since no cation $\Delta_tG°$ values were included in ref 1 for these aqueous/organic mixtures, reliance for splitting electrolyte data, not done according to the TATB convention by the authors, was made by using the potassium salt data and K^+ values derived from Bhattacharya et al.[39] on the TATB assumption.

3.6. Transfer to Aqueous 1,2-Ethanediol

The higher permittivity of 1,2-ethanediol (EG) than those of the three foregoing solvents permitted $\Delta_tG°(A^{n-},W\rightarrow W+EG)$ data to be obtained over the entire composition range, albeit only for the halides, picrate, and tetraphenylborate (Table 6). No data are available for any other ions, except for sulfate in very water-rich mixtures, but without any indication of the convention employed to obtain the individual ionic value.[40] The value $\Delta_tG°(SO_4^{2-})$/kJ mol^{-1} = 4.3 may be calculated for $x_{EG} = 0.1$ from the reported data. The self-consistency of the entries for Cl^- and Br^- is sufficiently good (although there are some wide variations at high x_{EG}) for sets of values to be recommended. The data from Elsemongy and Abdel-Khalek[41] for I^-, on the other hand, are consistently low and had to be rejected from the averages. The sets shown for I^- and for F^- (where only two independent value sets were reported) are marked as tentative.

3.7. Transfer to Aqueous 1,2-Propanediol

As expected, fewer data were reported for transfer into aqueous 1,2-propanediol (PG) than to aqueous EG, and the

Table 6. Standard Molar Gibbs Energies of Transfer of Anions from Water to 1,2-Ethanediol (EG) + Water Mixtures at 298.15 K, $\Delta_tG°$(ion)/kJ mol^{-1}, Molarity Scale

	$\Delta_tG°$(ion)/kJ mol^{-1} at the following values of $100x_{EG}$											
	10	20	30	40	50	60	70	80	90	100	method	ref
F^-	3.3	5.6	7.5	9.0	10.3	11.5	12.7	14.0	15.6	17.6	TATB	*a*
	2.8	4.6	6.0	7.3	9.0	9.5	10.0	10.5	13.0	14.0	Li^+, Na^+	*b*
	3.3	**5.1**	**6.7**	**8.2**	**{9.0}**	**10.6**	**11.5**	**12.3**	**14.1**	**15.8**	**TATB**	**T**
Cl^-	1.7	2.4	2.9	3.5	4.3	4.6	4.9	5.1	6.2	7.4	Na, K^+	4
	2.1	3.2	4.4	5.8	6.7	7.5	8.7	9.7	10.8	12.4	H^+	*c*
	1.5	2.9	(4.1)	5.3	(6.3)	(7.3)	8.2	9.1		10.9	TATB	*d*
	1.5	2.9	(4.1)	5.3	(6.3)	(7.3)	8.2	9.1		10.9	TATB	58
	1.0	1.5	2.0	2.9	3.2	3.6	4.3	4.8	5.5	6.8	H^+	*e*
	2.0	3.1	4.3	5.5	6.6	7.6	8.3	8.9	10.1	11.2	Li^+, Na^+, K^+	*f*
	1.5	**2.3**	**3.0**	**3.9**	**4.3**	**5.3**	**5.9**	**6.4**	**7.3**	**8.4**	**TATB**	**R**
Br^-	1.1	1.4	1.7	2.0	2.6	2.8	2.8	2.9	3.7	4.8	Na, K^+	4
	1.5	2.3	3.2	4.4	5.1	5.7	6.7	7.5	8.5	9.8	H^+	*c*
	0.7	1.1	1.6	2.1	2.7	3.3	3.9	4.7	5.4	6.4	TATB	*d*
	1.0	1.5	2.2	3.1	3.6	4.0	4.8	5.3	6.0	6.9	H^+	*e*
	1.7	2.2	3.0	4.1	5.0	5.4	5.7	6.0	6.9	8.1	K^+	*f*
	1.1	**1.6**	**2.1**	**2.8**	**3.5**	**3.9**	**4.3**	**4.8**	**5.5**	**6.6**	**TATB**	**R**
I^-	0.4	0.3	−0.3	0.0	0.2	−0.1	−0.5	0.0	1.4	4.8	Li^+	4
	0.1	−0.1	−0.1	−0.1	0.1	0.5	0.9	1.5	2.2	3.3	TATB	*d*
	[−0.2]	[−0.5]	[−0.6]		[−0.6]	[−1.0]	[−1.0]	[−1.1]	[−0.6]	[1.1]	H^+	41
	0.9	0.9	1.2	1.9	2.6	2.7	2.8	2.9	3.8	4.9	K^+	*f*
	0.5	**0.4**	**0.3**	**0.6**	**0.9**	**1.1**	**1.2**	**1.5**	**2.5**	**4.3**	**TATB**	**T**
Pic^-	−0.7	−1.7	−2.6	−3.5	−4.2	−4.9	−5.5	−6.0	−6.4	−6.8	TATB	*d*
BPh_4^-	−4.3	−7.8	−10.8	−13.5	−15.9	−17.8	−19.3	−20.4	−21.2	−21.7	TATB	*d*

[a] Hefter, G. T.; McLay, P. J. *J. Solution Chem.* **1988**, *17*, 535. [b] Senanayake, G.; Hefter, G. *Monatsh. Chem.* **2003**, *134*, 669. [c] Kundu, K. K. *Indian J. Chem.* **1972**, *10*, 303. [d] Das, A. K.; Kundu, K. K. *Indian J. Chem. A* **1978**, *16A*, 467. [e] Elsemongy, M. M.; Fouda, A. S. *J. Chem. Thermodyn.* **1982**, *14*, 1. [f] Elsemongy, M. M. *Thermochim. Acta* **1986**, *103*, 387.

Table 7. Standard Molar Gibbs Energies of Transfer of Anions from Water to 1,2-Propanediol (PG) + Water Mixtures at 298.15 K, $\Delta_tG°$(ion)/kJ mol^{-1}, Molarity Scale

	$\Delta_tG°$(ion)/kJ mol^{-1} at the following values of $100x_{PG}$													
	5	10	15	20	30	40	50	60	70	80	90	100	method	ref
Cl^-	1.5	2.8	3.9			8.4			13.0			19.2	H^+ *	42
		2.6		4.2	5.8	7.5	8.7	9.9	11.6			18.4	H^+ *	43
	1.5	2.7	3.8	4.7	(6.1)								H^+ *	44
Br^-	1.3	2.3	3.3			7.1			11.2			17.2	H^+ *	42
		2.1		3.4	4.6	6.1	7.1	8.1	9.7			16.1	H^+ *	43
	1.1	2.0	2.9	3.7	(5.3)								H^+ *	44
I^-	1.0	1.9	2.6			3.8			5.1			13.3	H^+ *	42
		1.4		2.1	2.9	4.0	4.7	5.5	6.8			12.5	H^+ *	43
	0.7	1.3	1.9	2.4	(3.6)								H^+ *	44
ClO_4^-	1.1	1.8	2.3	2.6	3.0	3.0	2.7	2.3	1.9	1.7	1.6	2.0	TATB	*a*
	[−2.8]	[−5.4]	[−8.1]	[−10.8]									Cs^+	44
Pic^-	−0.7	−1.3	−2.0	−2.7	−4.0	−4.9	(−5.2)	(−4.9)	−4.1			−3.7	TATB	*b*
BPh_4^-	−2.9	−5.5	−7.5	−9.2	−11.7	−13.4	(−15)	(−16)	−17.5			−19.5	TATB	*b*
	−3.8	−6.6	−9.1	−11.2	−14.6	−16.9	−18.5	−19.6	−20.7	−21.0	−21.8	−22.9	TATB	*a*

*The value of $\Delta_tG°(H^+,H_2O \rightarrow H_2O+EG)$ was used, due to inapplicable values from ref 1 for transfer into aqueous PG. [a] Panateova, T. D.; Krasnoperova, A. P. *Zh. Fiz. Khim.* **1992**, *66*, 593; *Russ. J. Phys. Chem.* **1992**, *66*, 313. [b] Sastry, V. V.; Kalidas, J. *Indian J. Chem. A* **1985**, *24A*, 811.

Table 8. Standard Molar Gibbs Energies of Transfer of Anions from Water to Glycerol (Gly) + Water Mixtures at 298.15 K, $\Delta_tG°$(ion)/kJ mol^{-1}, Molarity Scale

	$\Delta_tG°$(ion)/kJ mol^{-1} at the following values of $100x_{Gly}$							
	2	5	10	15	20	30	method	ref
Cl^-	−0.2	−0.3	−0.3	−0.1	0.0	0.1	TATB	45
	0.3	0.5	0.9	1.3	1.6	2.3	$H^{+\,a}$	*a*
Br^-	−0.2	−0.4	−0.6	−0.8	−0.8	−0.8	TATB	45
I^-	−0.4	−0.9	−1.4	−1.8	−2.1	−2.6	TATB	45
CN^-	−0.1	−0.1	0.3	0.8	1.4		K^+ *	*b*
Pic^-	−0.5	−1.0	−1.5	−1.9	−2.2	−2.9	TATB	45
	−0.2	−0.5	−1.1	−1.7			TATB	*c*
BPh_4^-	−0.6	−1.3	−2.1	−2.7	−3.2	−4.1	TATB	45
	−0.4	−0.9	−1.7	−2.2			TATB	*c*

*The H^+ and K^+ values are from ref 45 on the TATB assumption. [a] Elsemongy, M. M. *J. Electroanal. Chem.* **1978**, *90*, 77. [b] Blandamer, M. J.; Burgess, J.; Duffield, A. J. *J. Chem. Soc., Dalton Trans.* **1980**, 1. [c] Talukdar, H.; Rudra, S.; Kundu, K. K. *Can. J. Chem.* **1989**, *67*, 321.

recalculated values of those that have been reported are shown in Table 7. A difficulty encountered with these aqueous/organic mixtures regarding the halide anions is the apparent incorrectness of the $\Delta_tG°(H^+,W \rightarrow W+PG)$ data in ref 1, traceable to Dash et al.[40] and obtained from using the ferrocene−ferricinium (Fc) assumption. However, $\Delta_tG°(H^+A^-,W \rightarrow W+PG)$ could be reconstituted from the reported[42−44] $\Delta_tG°(H^+,W \rightarrow W+PG)$ and $\Delta_tG°(A^-,W \rightarrow W+PG)$ values for the hydrohalic acids. These were then split by assuming that the much more reliable $\Delta_tG°(H^+,W \rightarrow W+EG)$ values in ref 1, though still tentative, represent $\Delta_tG°(H^+,W \rightarrow W+PG)$ fairly well enough. Unfortunately, no values using the TATB method were reported for the halide anions, so no adjustment for small deviations caused by using the EG values for the PG ones could be made. The values reported for $CsClO_4$ by Wells[44] lead to improbable, quite negative values of $\Delta_tG°(ClO_4^-)$ that are rejected, although the $\Delta_tG°(Cs^+)$ values in ref 1, on which the anion values are based and that were obtained with the TATB assumption, are reasonable.

3.8. Transfer to Aqueous Glycerol

Although glycerol (Gly) is miscible with water and has a high permittivity, the reported $\Delta_tG°(A^-,W \rightarrow W+Gly)$ data (Table 8) pertain only to rather water-rich mixtures, possibly because of the high viscosity of the cosolvent-rich ones. The hydrogen bond donating ability of glycerol, even in its aqueous mixtures, leads to negative $\Delta_tG°(A^-)$ values. Exceptions are two sets of data, one for Cl^- and one for CN^-, not obtained using the TATB assumption directly. In fact, no $\Delta_tG°$(cation) data for aqueous glycerol were included in ref 1 because of the paucity of the published data. For the above-mentioned two sets, the H^+ and K^+ values from Basumalik and Kundu[45] obtained with the TATB assumption were, therefore, used with the HCl and KCN data, but the $\Delta_tG°$(cation) could not be critically evaluated. Hence, they are less reliable, but even here the resulting positive $\Delta_tG°$(anion) values are not large.

These eight tables summarize the information available of the Gibbs energies of transfer of anions into aqueous mixture of protic solvents—alkanols in an extended meaning—except for data listed further below on transfer into aqueous formamide. The following tables deal with transfer of anions into aqueous mixtures of polar aprotic solvents.

3.9. Transfer to Aqueous Tetrahydrofuran

The reported data for transfer of anions into aqueous tetrahydrofuran (THF), $\Delta_tG°(A^-,W \rightarrow W+THF)$, are summarized in Table 9, pertaining to rather water-rich mixtures only. Here, as for transfer into other aqueous mixtures with cosolvents having low permittivities, ion pairing and unknown activity coefficient corrections prevent the evaluation of the $\Delta_tG°$(anion) values beyond $x_{THF} \sim 0.2$. Even so, data are available for only very few anions, but for two of them, Cl^- and Br^- reports, from sufficiently diverse sources, permit the averaging and the selection of tentatively recommended values. These are only tentative, since the $\Delta_tG°$(cation) values that have been used in their evaluation, although based on the TATB assumption, were unconfirmed by additional, independent studies.

Although for these two anions the values from Datta and Kundu[46] and Elsemongy and Abdel-Khalek[47] differ by no more than 3 kJ mol^{-1}, the difference is much larger for I^-, and there are no additional data to decide between these two sets.

3.10. Transfer to Aqueous 1,4-Dioxane

The reported data for transfer of anions into aqueous 1,4-dioxane (Diox), $\Delta_tG°(A^-,W \rightarrow W+Diox)$, are summarized in Table 10, pertaining to rather water-rich mixtures only. What

Table 9. Standard Molar Gibbs Energies of Transfer of Anions from Water to Tetrahydrofuran (THF) + Water Mixtures at 298.15 K, $\Delta_t G°$(ion)/kJ mol^{-1}, Molarity Scale

	$\Delta_t G°$(ion)/kJ mol^{-1} at the following values of $100x_{THF}$						
	2	5	10	15	20	method	ref
OH^-	4.0	8.1	11.4	15.3	19.1	H^+	*a*
Cl^-	3.4	6.9	10.6	14.1	16.2	H^+, Rb^+	37
	2.8	5.9	9.6	11.8	12.2	H^+	46
	3.1	5.9	8.9	10.4	11.2	M^+ *	*b*
	2.8	6.5	8.6	11.8		H^+	*a*
	3.3	6.7	10.3	12.9	15.0	M^+ *	47
	3.1	**6.4**	**9.6**	**12.2**	**13.7**	**TATB**	**T**
Br^-	2.3	4.7	7.4	9.1	9.6	H^+	46
	2.3	4.7	6.6	7.6	7.6	H^+	*c*
	2.5	4.8	6.9	9.9	10.8	H^+	*a*
	3.0	5.8	8.7	10.9	12.6	M^+ *	47
	2.5	**5.0**	**7.4**	**9.4**	**10.2**	**TATB**	**T**
I^-	1.5	2.8	3.9	3.8	2.6	H^+	46
	2.6	4.9	7.2	8.7	10.0	M^+ *	47

*Average of using Li^+, Na^+, K^+, and Rb^+ from Bhattacharya et al.[b] as reported in ref 1. [a] Sidahmed, I. M.; Wells, C. F. *J. Chem. Soc., Faraday Trans. 1* **1987**, *83*, 439. [b] Bhattacharya, A.; Datta, J.; Das, K.; Kundu, K. K. *Indian J. Chem. A* **1982**, *21A*, 9. [c] Elsemongy, M. M.; Kennawy, I. M.; Fouda, A. *J. Chem. Soc., Faraday Trans. 1* **1982**, *78*, 1257.

Table 10. Standard Molar Gibbs Energies of Transfer of Anions from Water to 1,4-Dioxane (Diox) + Water Mixtures at 298.15 K, $\Delta_t G°$(ion)/kJ mol^{-1}, Molarity Scale

	$\Delta_t G°$(ion)/kJ mol^{-1} at the following values of $100x_{Diox}$					
	5	10	15	20	method	ref
OH^-	6.2	10.5	11.8		$Me_4N^{+\dagger}$	*a*
Cl^-	4.8	9.0	10.6		K^+	*b*
	6.0	9.3	10.2	13.1	M^+ **	*a*
	5.1	8.4	9.8		H^+, Rb^+	37
	3.9	6.9	8.3		H^+	48
	5.0	8.1	9.0	7.7	H^+	46
	4.1	6.6	7.2	9.5	H^+	*c*
	4.1	6.8	7.9	(12.4)	M^+ *	*d*/*e*
	4.8	8.1	9.8	12.9	H^+	49
	5.0	**8.3**	**9.5**	**(11)**	**TATB**	**T**
Br^-	2.6	4.2	5.2		M^+ **	*a*
	3.2	5.2	5.6		H^+	48
	4.3	6.6	6.7	4.6	H^+	46
	4.1	6.8	7.7	10.0	H^+	49
	3.6	**5.7**	**6.3**		**TATB**	**T**
I^-	−2.0	−3.1	−2.6		H^+	48
	−3.0	−4.4	−3.8	−1.4	H^+	46
	3.1	4.8	4.6	5.8	H^+	49
CN^-	2.6	4.4	3.9			*f*
SCN^-	−2.5	−3.7	−3.1		H^+	50
BPh_4^-	−11.8	−19.9	−25.7		M^+ **	*a*
WO_4^{2-}	[−7.0]	[3.8]	[20.8]		?	51
PO_4^{3-}	[15.6]	[19.0]	[23.6]		?	51
AsO_4^{3-}	[4.0]	[8.3]	[9.3]		?	51

*Average of using Li^+, Na^+, K^+, Rb^+, and Cs^+ from ref 1. **Average of using Li^+, Na^+, and Ph_4P^+ and TPTB. † Using Cl^-,[b] Me_4NCl, and Me_4NOH data. [a] Rat, J. C.; Villermaux, S.; Delpuech, J. J. *Bull. Soc. Chim. Fr.* **1974**, 815. [b] Bax, D.; Alfenaar, M.; DeLigny, C. L. *Recl. Trav. Chim.* **1971**, *90*, 1002. [c] Elsemongy, M. M.; Fouda, A. S. *Electrochim. Acta* **1981**, *26*, 255. [d] Bhattacharya, A.; Datta, J.; Das, K.; Kundu, K. K. *Indian J. Chem. A* **1982**, *21A*, 9. [e] Feakins, D.; Hickey, B. E.; Lorimer, J. P.; Voice, P. I. *J. Chem. Soc., Faraday Trans. 1* **1975**, *71*, 780. [f] Blandamer, M. J.; Burgess, J.; Duffield, A. J. *J. Chem. Soc., Dalton Trans.* **1980**, 1.

Table 11. Standard Molar Gibbs Energies of Transfer of Anions from Water to 1,2-Dimethoxyethane (DME) + Water Mixtures at 298.15 K, $\Delta_t G°$(ion)/kJ mol^{-1}, Molarity Scale

	$\Delta_t G°$(ion)/kJ mol^{-1} at the following values of $100x_{DME}$						
	2	5	10	15	20	method	ref
F^-	3.1	7.1	12.9	17.4	20.6	H^+ *	52
Cl^-	2.3	5.4	9.8	13.2		TATB	53
	2.2	5.1	9.2	12.4	14.7	H^+ *	52
Br^-	1.5	3.6	7.1	10.5		TATB	53
	1.6	3.8	7.2	10.5	13.5	H^+ *	52
I^-	0.8	2.1	4.2	6.1		TATB	53
	0.9	2.2	4.4	6.6	8.9	H^+ *	52
Pic^-	0.4	0.6	0.2	−1.1		TATB	53
	0.6	1.0	1.3	0.9	−0.2	H^+ *	52
$PhCO_2^-$	2.3	4.7	7.2	8.3	9.2	H^+ *	69
BPh_4^-	−5.0	−10.6	−17.9	−22.7		TATB	53
	−4.1	−8.7	−14.9	−19.5	−22.4	H^+ *	52

*The $\Delta_t G°(H^+)$ values were obtained from an indicator method by Wells.[52]

was said concerning this limitation for aqueous THF is valid here, too. Again, there are sufficient data reported from diverse sources for two anions, Cl^- and Br^-, to permit the averaging and the selection of tentatively recommended values. More reliance may be placed on the $\Delta_t G°$(cation) values, in particular $\Delta_t G°(H^+)$, needed for evaluation of the $\Delta_t G°$(anion) values than in the case of transfer into aqueous THF, because the former have been better substantiated in ref 1. The rather roundabout manner by means of which the values for $\Delta_t G°(OH^-)$ were obtained appears not to detract from the reliability of the latter, in view of the values for Cl^- and Br^-.

The negative $\Delta_t G°(I^-)$ values obtained from Datta and Kundu[46] and Mishra et al.[48] contrast with the positive values from Elsemongy and Abu Elnader,[49] with the latter being in better harmony with the values for Cl^- and Br^-. However, $\Delta_t G°(SCN^-)$ from Das and Das[50] is also negative and SCN^- is a large anion like I^-, so that negative values for these two anions are not completely unreasonable. No details were published on how the values reported by Dash and Padhi[51] for the multivalent anions WO_4^{2-}, PO_4^{3-}, and AsO_4^{3-} were arrived at nor on why the values for the latter two differ considerably. These data ought to be considered as unreliable.

3.11. Transfer to Aqueous 1,2-Dimethoxyethane

The reported data for transfer of anions into the third aqueous ether system for which data are available, aqueous 1,2-dimethoxyethane (DME), $\Delta_t G°(A^-,W \rightarrow W+DME)$, are summarized in Table 11, pertaining again to water-rich mixtures only. Sets of values of $\Delta_t G°$(anion) were reported by two sources,[52,53] but those from Wells[52] were based on $\Delta_t G°$(electrolyte) data reported by other authors (the references given to their work were wrong, however). The splitting of the latter to yield $\Delta_t G°$(anion) was made by means of the use of an indicator method developed by Wells[54] yielding $\Delta_t G°(H^+)$ values, and then, via $\Delta_t G°(HCl)$, $\Delta_t G°(Cl^-)$ and values for other cations and anions. Although the results agree on the whole with values obtained by means of the TATB assumption,[53] they cannot be used as an independent corroboration of them.

3.12. Transfer to Aqueous Acetone

A considerably larger body of information is available for the transfer of anions to aqueous acetone (Me_2CO) than that for transfer into the aqueous ethers reviewed above. The recalculated values of $\Delta_t G°(A^-,W \rightarrow W+Me_2CO)$ are reported in Table 12, dealing on the whole with higher cosolvent concentrations than those for the aqueous ethers, though not reaching acetone-rich compositions. The values for the halides that were reported from several sources in good mutual agreement could be averaged, and recommended values could be presented (with those for fluoride

Table 12. Standard Molar Gibbs Energies of Transfer of Anions from Water to Acetone (Me_2CO) + Water Mixtures at 298.15 K, Δ_tG°(ion)/kJ mol^{-1}, Molarity Scale

	Δ_tG°(ion)/kJ mol^{-1} at the following values of $100x_{Me_2CO}$							
	10	20	30	40	50	60	method	ref
OH^-	7.1	12.8	17.1	20.1			H^+	*a*
	11.4	19.1	26.0				H^+	5
F^-	10.4	18.2	23.1				Na^+	*b*
	10.2	18.0					K^+ *	*c*
	8.9	17.5	22.1	29	34	41	Li^+, Na^+	72
	9.7	**17.8**	**22.6**	**{29}**	**{34}**	**{41}**	**TATB**	**T**
Cl^-	7.6	13.7	18.7	22.7	25.6	27.5	K^+	*d*
	7.6	13.7	18.7	22.5	26.1	30.0 **	H^+, Rb^+	37
	7.7	13.9	18.3				H^+	5
	7.7	14.0	18.7				M^{+} †	*b*
	7.7	13.2	17.6	21.6	25.9		TATB	55
	7.9	14.4	19.6	23.6	26.4		K^+	*e*
	7.5	13.5	18.2	22.1	25.1	28.3	M^{+} †	*f*
	[3.7]	[7.4]	[9.8]	[11.5]	[12.5]	[13.1]	see text	20
	8.0	13.6	18.4	21.7	25.0	28.4	K^+	*g*
	7.7	**13.9**	**18.8**	**22.7**	**25.8**	**28.5**	**TATB**	**R**
Br^-	6.4	11.6	15.8	19.1	21.6	23.2	K^+	*d*
	6.4	11.7	15.4				Na^+	*b*
	6.7	12.5	17.5	21.9	25.5		K^+	*e*
	6.2	11.2	14.8	18.4	20.6	23.1	Na^+	*f*
	6.4	**11.7**	**15.9**	**19.8**	**22.6**	**22.6**	**TATB**	**R**
I^-	4.6	8.1	10.9	13.0	14.3	14.9	K^+	*d*
	4.6	8.1	(10.0)				Na^+	*b*
	5.0	9.2	12.6	15.1	16.7		K^+	*e*
	4.4	7.8	10.1	12.5	13.6	15.2	Na^+	*f*
	4.6	**8.3**	**10.9**	**12.8**	**14.0**	**14.4**	**TATB**	**R**
CN^-	4.8	9.7	13.9	16.5	18.3	23.2	K^+	*h*
	5.1	9.3	12.9	16.0	18.6	22.1	K^+	*e*
SCN^-	3.6	6.6	9.2	11.4	13.2		K^+	*e*
NO_3^-	5.7	9.5	12.7	16.6			TATB	55
ClO_3^-	5.2	8.9	11.6	13.8	16.1		TATB	55
ClO_4^-	3.2	5.0	5.7	5.8	5.8	5.8	K^+	*d*
	1.7	2.3	2.4	2.5	2.7	3.6 **	TATB	55
	2.2	3.6	4.4	5.0	5.5	7.6	K^+	*e*
MnO_4^-	0.8	0.7	0.1	−0.5	−0.9	−0.7 **	TATB	55
BPh_4^-	−5.9	-11.6	−16.7	−21.8	−25.9	−28.7	K^+	*d*
	−6.6	−12.3					TATB	55
CO_3^{2-}	16.9	27.6					TATB	55
SO_4^{2-}	23.3	39.1					TATB	55
HPO_4^{2-}	17.8	35.3					TATB	55
$S_2O_6^{2-}$	14.5	25.7	34.0	39.7			TATB	55
$S_2O_8^{2-}$	8.7	15.3	20.6	25.1	29.6		TATB	55
$Cr_2O_7^{2-}$	9						TATB	55

*The $\Delta_tG^\circ(K^+)$ is stated to be taken from Blandamer et al.;[e] this differs somewhat from that established in ref 1. **Value also at $x_{Me_2CO} = 0.7$: Cl^-, 33.4; ClO_4^-, 5.3; MnO_4^-, −0.5. † Average of using Li^+, Na^+, K^+, Rb^+, and Cs^+ from ref 1. [a] Gillet, H.; Avedikian, L.; Morel, J.-P. *Can. J. Chem.* **1975**, *53*, 455. [b] Feakins, D.; Knox, M.; Hickey, B. E. *J. Chem. Soc., Faraday Trans. 1* **1984**, *80*, 961. [c] Hefter, G. T. *Rev. Inorg. Chem.* **1989**, *10*, 185. [d] Bax, D.; DeLigny, C. L.; Remijnse, A. G. *Recl. Trav. Chim.* **1972**, *91*, 965. [e] Blandamer, M. J.; Briggs, B.; Burgess, J.; Guardado, P.; Radulovich, S.; Hubbard, C. D. *J. Chem. Soc., Faraday Trans. 1* **1988**, *84*, 1243. [f] Elsemongy, M. M.; Abdel-Khalek, A. A. *Can. J. Chem.* **1989**, *67*, 1268. [g] Parfenyuk, V. A.; Chankina, T. I. *Mendeleev Commun.* **2005**, 212. [h] Blandamer, M. J.; Burgess, J.; Duffield, A. *J. Chem. Soc., Dalton Trans.* **1980**, 1.

being tentative only). The value for Cl^- derived from “real” electrochemical potentials via eq 7 suffers from the same problems already discussed in section 3.1 for methanol solutions; hence, it is considered unreliable and is rejected. For CN^- the two sets of values that are in good agreement come from the same laboratory, so they cannot be said to be independently confirmed. The values for the divalent anions originate from curves in figures[55] and may be less precise than numerical values reported for the univalent anions.

3.13. Transfer to Aqueous Ethylene Carbonate

Ethylene carbonate (EC) is completely miscible with water, but its melting point is 309.5 K. Therefore, transfer of electrolytes or ions from water into aqueous EC at 298.15 K is limited to water-rich compositions, up to ca. $x_{EC} = 0.4$, whereas the entire composition range can be (and was[56]) studied at 313.15 K. On the other hand, propylene carbonate (PC) is liquid at 298.15 K and many Δ_tG°(ion,W→PC) data are well established[12] at this temperature, but it is immiscible with water. Transfer of ions into aqueous mixtures of PC is therefore limited to a very narrow range of dilute solutions in water[56,57] and is not discussed here further. Ethylene carbonate has a high permittivity, similar to that of water, and solutions of electrolytes in neat EC and its aqueous mixtures should be relatively easy to study, but unfortunately only very few authors took the trouble of doing so. The available Δ_tG°(A^-,W→W+EC) data are presented in Table 13.

The Δ_tG°(A^-,W→W+EC) data at 313.15 K reported by Cabon et al.[56] for the halide and triiodide anions derive from solubility data of the silver salts, and the value for Δ_tG°(Ag^+,W→W+EC) was based on electrochemical measurements employing the ferrocene−ferricinium (Fc) extrathermodynamic assumption. This assumption is incompatible with the TATB assumption employed throughout this review, as also for transfer into aqueous EC as measured by Sinha and Kundu.[57] Large differences were noted by Kundu and Parker[58] between results based on these two assumptions in the cases of aqueous acetonitrile and dimethyl sulfoxide (see also ref 1), so it is to be expected that such differences would prevail for the similarly dipolar aprotic EC too. Two of the sets of data for Cl^- transfer at 298.15 K into water-rich mixtures[57,59] are in mutual agreement but differ considerably from a third one,[60] which is also incompatible with the data for F^- and the expected gradation in the $\Delta_tG^\circ(A^-)$. The data for ClO_4^-, derived from the solubilities of $KClO_4$ in the mixtures reported by Grančičovà[61] employing $\Delta_tG^\circ(K^+)$ from Sinha and Kundu[57]and the TATB assumption, are at variance with the values of $\Delta_tG^\circ(ClO_4^-)$ shown in that paper[61] and nominally also derived from the same $\Delta_tG^\circ(K^+)$, but no reason was presented for this discrepancy.

3.14. Transfer to Aqueous Acetonitrile

The transfer of anions into aqueous acetonitrile (MeCN) has been studied much more extensively than that into other aqueous solvents, and the resulting Δ_tG°(A^-,W→W+MeCN) data are shown in Table 14.

Sufficiently diverse sources reported data for the transfer of Cl^- to permit averaging (excluding the set of data from Gomaa[62] that are much too positive even in dilute MeCN) and providing a set of recommended data. The situation is less favorable concerning the other halide anions, however, in that only two or three sets of data for each anion are available, and these are not in good mutual agreement, even when the data of Gomaa[62] for water-rich mixtures are excluded. The latter data cannot be correct, because they report highly positive Δ_tG° values for even extremely dilute solutions of acetonitrile in water. For acetonitrile-rich mixtures, however, the Gomaa data[62] do not differ as much from the other sets of data (one set for Br^- and one for I^-). For BPh_4^- the diverse data sets could be averaged, when that due to Cox et al.[63] was excluded, and a recommended set could be presented. It is noteworthy that this excluded set, depending on the $\Delta_tG^\circ(K^+)$ from ref 1, leads to not sufficiently negative values for $\Delta_tG^\circ(BPh_4^-)$, i.e., too high values; sets of data depending on the same $\Delta_tG^\circ(K^+)$ values lead to apparently too low positive values in the cases of

Table 13. Standard Molar Gibbs Energies of Transfer of Anions from Water to Ethylene Carbonate (EC) + Water Mixtures at 298.15 K (Roman Numbers) and 313.15 K (*Italic* Numbers), $\Delta_t G°$(ion)/kJ mol^{-1}, Molarity Scale

	$\Delta_t G°$(ion)/kJ mol^{-1} at the following values of 100x_{EC}													
	5	10	15	20	30	40	50	60	70	80	90	100	method	ref
F^-	6.4	10.6	12.3	12.8									Na^+ *	*a*
Cl^-		*4.5*		*8.6*	*12.0*	*14.6*	*16.6*	*18.2*	*20.2*	*23.3*	*28.4*	*36.7*	Fc	56
	4.5	8.3	11.3	13.8	18.2	20.4							H^+ *	*b*
	2.8	5.0	6.7	7.5									H^+ *	59
	2.3	4.3	5.9	7.1	8.2								TATB	57
Br^-	2.5	4.7	6.6	8.3	12.3								H^+ *	*c*
	2.0	*3.9*	*5.4*	*6.8*	*10.0*								H^+ *	*c*
		4.4		*7.8*	*10.5*	*12.7*	*14.6*	*16.5*	*18.7*	*21.2*	*24.3*	*28.2*	Fc	56
I^-	0.4	0.6	0.9	1.5	4.4								H^+ *	*c*
	0.2	*0.3*	*0.5*	*1.0*	*2.3*								H^+ *	*c*
		2.8		*4.9*	*6.3*	*7.5*	*8.8*	*10.3*	*12.1*	*14.1*	*16.2*	*18.2*	Fc	56
I_3^-		*5.9*		*9.8*	*12.3*	*14.0*	*15.0*	*15.5*	*15.8*	*15.9*	*15.9*	*15.7*	Fc	56
ClO_4^-	−2.2	−3.6	−4.7	−5.5									K^+ *	61
$PhCO_2^-$	*0.6*	*1.6*	*2.4*	*3.7*	*6.1*								H^+ **	*d*
Pic^-	−3.0	−5.4	−7.3	−8.7	−10.3								TATB	57
BPh_4^-	−8.7	−11.5	−21.5	−25.7	−29.6								TATB	57

*From $\Delta_t G°$(electrolyte) using $\Delta_t G°$(cation) from ref 57. **At 308.15 K rather than 313.15 K. [a] Hernandez-Luis, F.; Vazquez, M. V.; Esteso, M. A. *Fluid Phase Equilib.* **2004**, *218*, 295. [b] Elsemongy, M. M.; Fouda, A. S. *Electrochim. Acta* **1981**, *26*, 1125. [c] Sinha, S.; Rudra, S.; Kundu, K. K. *Indian J. Chem. A* **1993**, *32A*, 1. [d] Sinha, S.; Rudra, S.; Kundu, K. K. *Indian J. Chem. A* **1993**, *32A*, 12.

Table 14. Standard Molar Gibbs Energies of Transfer of Anions from Water to Acetonitrile (MeCN) + Water Mixtures at 298.15 K, $\Delta_t G°$(ion)/kJ mol^{-1}, Molarity Scale

	$\Delta_t G°$(ion)/kJ mol^{-1} at the following values of 100x_{MeCN}											
	10	20	30	40	50	60	70	80	90	100	method	ref
F^-	3.3	6.6	13.0	17.0		23.4	28.3	32.3	39.0	45	TATB	*a*
	7.2	18.5	24.3	28.3	31.1	34.8	39.3	38.2	43.7	49.3	H^+ ††	*b*
Cl^-	4.3	6.0	9.6	11.4	13.6	16.1	19.5				H^+, Rb^+	37
	4.4	6.8	8.8	10.9	14.3	18.8	24.6	31.5	38.2	44.0	M^+ *	63
	3.3	5.3	7.1	8.5	10.1	11.7	13.4				M^+ **	64
	3.9	6.6	8.6	10.4	12.5	(15.2)	19.0	24.5		41.9	TATB	21
	[11.5]	[18.5]	[23.3]	[26.4]	[28.5]	[29.9]	[31.2]	33.1	35.9	40.3	TATB	62
	2.5	4.8	6.5	7.9	8.8	9.3					see text	20
	5.5	7.2	9.1	10.1	12.7	14.3					see text	*c*
	4.0	**6.0**	**8.5**	**10.3**	**12.7**	**17.5**		**{32.3}**	**[37.1}**	**42.1**	**TATB**	**R/T**
Br^-	3.4	5.9	7.7	9.6	12.0	15.2	19.4	25.0	28.9	33.0	M^+ *	63
	3.1	3.9	4.9	5.5	7.3	8.9	10.2				K^+	64
	[9.4]	[15.0]	[18.8]	[21.2]	[22.5]	[23.0]	[23.1]	23.2	23.6	24.7	TATB	62
I^-	1.9	1.8	1.8	1.6	2.7	3.8	4.6				K^+	64
	2.3	4.2	5.5	6.4	7.7	9.2	11.1	14.0	16.9	20.3	M^+ *	63
	[8.7]	[10.9]	[10.4]	[8.9]	7.9	8.2	10.0	13.1	16.5	18.9	TATB	62
SCN^-	{22.6}	{22.6}	{24.3}			28.5	31.0		36.8	38.5	TATB	*d*
ClO_3^-	0.5	1.3									TATB	*e*
BrO_3^-	2.4	7.6	10.3	12.4	14.0	16.2	19.4	23.3	28.3	33.5	Ag^+ †	*f*
	1.6	2.0									TATB	*e*
IO_3^-	4.6	10.9	14.3	17.0	19.8	23.1	27.2	30.7	31.4	31.5	Ag^+ †	*f*
	3.9	9.3									TATB	*e*
ClO_4^-	−0.6	0.9	1.0	0.6	0.7	1.4	2.1	3.3	4.8	6.3	K^+, Ag^+	*g*
	−2.3	0.0									TATB	*e*
HF_2^-			24.3		35.1	40.5	43.2		42.0	66.2	H^+ ††	*b*
$CH_3CO_2^-$	3.8	9.6	12.9	15.4	17.7	20.7	24.3	29.5	36.0	45.9	Ag^+ †	*h*
BPh_4^-	−12.4	−19.7	−24.2	−26.9	−28.7	−30.0	−31.3	−32.5	−33.5	−33.6	TATB	*i*
	[−6.8]	[−14.7]	[−20.7]	[−25.4]	[−27.3]	[−27.6]	[−25.2]	[−23.0]	[−21.0]	[−18.8]	K^+	63
	−11.6	−19.2	−23.8	−26.8	−28.9	−30.4	−31.6	−32.5	−33.3	−33.8	TATB	*j*
	−10.7	−18.9	−23.5	−26.2	−28.1	−29.7	−30.4	−31.3	−32.1	−32.9	TATB	58
	−11.7	−19.0	−24.0	−27.2	−29.1	−30.1	−30.6	−31.1	−32.1	−34.0	TATB	62
	−12.1	−21.0	−26.5	−28.5							TATB	*k*
	−11.7	**−19.6**	**−24.4**	**−27.1**	**−28.7**	**−30.1**	**−31.0**	**−31.9**	**−32.8**	**−33.6**	**TATB**	**R**

*Averages of using Li^+, Na^+, K^+, and Cs^+ for Cl^-; Na^+, K^+, and Ag^+ for Br^-; and K^+ and Ag^+ for I^-. **Average of using Li^+, Na^+, K^+, Rb^+, and Cs^+ from ref 1. † At 303.15 K for the silver salts, but 298.15 K for Ag^+ from ref 1. †† At 294.15 K for the dissociated acids, but 298.15 K for H^+ from ref 1. [a] Hefter, G. T.; McLay, P. J. *J. Solution Chem.* **1988**, *17*, 535. [b] Bessiere, J.; Bazine, F. *J. Fluorine Chem.* **1989**, *44*, 45. [c] Parfenyuk, V. A.; Chankina, T. I. *Mendeleev Commun.* **2005**, 212. [d] Giridhar, V. V.; Dalidas, C. *J. Solution Chem.* **1982**, *11*, 539. [e] Benko, J.; Vollarova, O. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 855. [f] Subramanian, S.; Rao, S. C. A. V. S. S.; Kalidas, C. *Indian J. Chem. A* **1981**, *A20*, 723. [g] Cox, B. G.; Guminski, C.; Schneider, H. *J. Am. Chem. Soc.* **1982**, *104*, 3789. [h] Subramanian, S.; Kalidas, C. *Trans. SAEST* **1984**, *19*, 265. [i] Kim, J.-I.; Cecal, A.; Born, H.-J.; Gomaa, E. A. *Z. Phys. Chem. (NF)* **1978**, *110*, 209. [j] Kim J.-I. *Z. Phys. Chem. (Munich)* **1980**, *121*, 1. [k] Talukdar, H.; Kundu, K. K. *J. Phys. Chem.* **1992**, *96*, 970.

the transfers of Br^- and I^- for the potassium salt data of Das et al.[64]

3.15. Transfer to Aqueous Formamide

With one exception, all the anion transfer data into aqueous formamide, $\Delta_t G°(A^-, W \rightarrow W+FA)$, are from one source, Suzuki.[65] The values (see Table 15) were derived from electrochemical measurements on solutions of salts in water and in aqueous formamide mixtures with an ion sensitive electrode based on 2,6-dinitrobenzene, which is immiscible with the protic solvents. The potentials were "referred to an imaginary potential denoted as TPhE, where the transfer Gibbs energy corresponds to zero based on the [TATB] extrathermodynamic assumption at a liquid|liquid inter-

Table 15. Standard Molar Gibbs Energies of Transfer of Anions from Water to Formamide (FA) + Water Mixtures at 298.15 K, $\Delta_t G°$(ion)/kJ mol^{-1}, Molarity Scale

	$\Delta_t G°$(ion)/kJ mol^{-1} at the following values of $100x_{FA}$											
	10	20	30	40	50	60	70	80	90	100	method	ref
F^-	7.7	14.5	18.5	23.1	27.3	31.0	34.4	37.5			Na^+	66
Br^-	2.6	3.6									TATB	65
I^-	2.6	3.6	3.8	3.6	3.4	3.3	3.4	3.6	3.6	3.3	TATB	65
ClO_3^-	4.2	5.6	5.9	6.0	6.2	6.4	5.5				TATB	65
NO_3^-	1.4	2.5	3.8								TATB	65
BF_4^-	−0.4	−0.6	−0.7	−0.8	−0.8	−0.8	−0.7	−0.6	−0.4	−0.2	TATB	65
ClO_4^-	−0.5	−0.8	−1.1	−1.3	−1.4	−1.5	−1.5	−1.5	−1.4	−1.3	TATB	65
IO_4^-	−0.5	−0.8	−1.1	−1.3	−1.4	−1.5	−1.5	−1.5	−1.4	−1.3	TATB	65
$CCl_3CO_2^-$	1.2	2.2	2.4	1.7	0.9	1.3	4.9				TATB	65
PF_6^-	−2.0	−3.0	−3.6	−4.2	−4.9	−5.9	−7.1	−8.1	−8.8	−8.4	TATB	65
Pic^-	−2.0	−3.5	−4.5	−5.3	−6.1	−7.0	−7.9	−8.8	−9.5	−9.6	TATB	65
BPh_4^-	−2.3	−3.9	−5.3	−6.5	−7.7	−9.0	−10.2	−11.2	−11.8	−11.6	TATB	65

Table 16. Standard Molar Gibbs Energies of Transfer of Anions from Water to *N*,*N*-Dimethylformamide (DMF) + Water Mixtures at 298.15 K, $\Delta_t G°$(ion)/kJ mol^{-1}, Molarity Scale

	$\Delta_t G°$(ion)/kJ mol^{-1} at the following values of $100x_{DMF}$											
	10	20	30	40	50	60	70	80	90	100	method	ref
OH^-	[−0.2]	[3.1]	[7.9]								H^+	67
F^-	9.0	18.0	26.0								K^+	73
Cl^-	5.9	12.4	17.7	21.1	24.2	29.2					H^+, Rb^+	37
	5.7	12.2	18.7								K^+	73
	4.9	10.6	15.1	18.1	20.6					38.7	M^+ *	*a*
	6.3	12.0	16.5	20.3	23.6	26.8				45.9	TATB	21
	2.8	7.9	12.4	13.3							H^+	*b*
	4.1										H^+	*c*
	5.2	10.9	15.9	18.2	20.4						K^+	*d*
	9.2	11.8	14.4	14.7	15.7	17.8	19.4	21.0	23.0		see text	*e*
	4.4	**9.5**	**13.8**	**16.1**	**18.1**						**TATB**	**R**
Br^-	4.2	8.9	13.1								K^+	68
	3.3	7.3	10.8	11.7	12.7					22.0	K^+	*a*
	0.6	4.1	9.0								H^+	*b*
I^-	2.0	4.4	6.3								K^+	68
	0.2	−0.6	−1.5	−0.2	0.6					11.1	K^+	*a*
IO_3^-	9.4	12.5	18.9	24.0	29.6	32.2	33.0	32.9	33.4	34.7	Cu^{2+}	*f*
HCO_2^-	8.2	9.4	12.0		13.6	10.7	10.3	9.8	9.7	9.7	Cu^{2+}	*f*
$PhCO_2^-$	0.5	5.7	8.1	11.6	10.8	10.4	9.2	7.2	6.9	5.9	Cu^{2+}	*f*
Pic^-	−1.3	−1.4	−1.7	−4.6	−7.4						K^+	*a*
	−3.7	−5.9	−8.0	−12.3	−16.2					−22.8	K^+	*d*
BPh_4^-	−11.0	−19.0	−24.8	−28.8	−31.7						TATB	*g*
	−10.4	−19.0	−25.7	−30.8	−34.5	−37.1	−39.1	−40.5	−41.8	−43.3	TATB	*h*
	−11.9	−20.4	−26.4	−29.7	−30.3						K^+	*d*
	−11.5	**−19.5**	**−25.6**	**−29.3**	**−31.0**						**TATB**	**R**

*Averages of using Li^+, Na^+, K^+, and Cs^+ for Cl^-; Na^+, K^+, and Ag^+ for Br^-; and K^+ and Ag^+ for I^-. [a] Das, K.; Bose, K.; Kundu, K. K. *Electrochim. Acta* **1981**, *26*, 479. [b] Rao, D. M.; Kalidas, C. *J. Chem. Eng. Data* **1987**, *32*, 158. [c] Sidahmed, I. M.; Wells, C. F. *J. Chem. Soc., Faraday Trans. 1* **1988**, *84*, 1153. [d] Ray, S. K.; Sarkar, S.; Sinha, S.; Kundu, K. K. *Indian J. Chem. A* **1994**, *33A*, 805. [e] Parfenyuk, V. A.; Chankina, T. I. *Mendeleev Commun.* **2005**, 212. [f] Varghese, V. V.; Kalidas, C. *J. Indian Chem. Soc.* **1993**, *70*, 311. [g] Kim, J.-I.; Cecal, A.; Born, H.-J.; Gomaa, E. A. *Z. Phys. Chem. (NF)* **1978**, *110*, 209. [h] Gomaa, E. A. *Thermochim. Acta.* **1989**, *142*, 19.

face".[65] There being no confirming—or disagreeing—results from other sources, it is not possible to evaluate the data further. The values for F^-, in order to be derived from the NaF salt transfer data from Hernandez-Luis et al.,[66] needed to depend on $\Delta_t G°(Na^+)$ from Suzuki.[65]

3.16. Transfer to Aqueous *N*,*N*-Dimethylformamide

Contrary to the case of anion transfer into aqueous formamide, several authors studied the Gibbs energy of transfer of anions into aqueous *N*,*N*-dimethylformamide (DMF), $\Delta_t G°(A^-, W \rightarrow W + DMF)$, and results are shown in Table 16. However, most of these authors abstained from providing data for mixtures with $x_{DMF} > 0.5$ up to neat DMF. Thus, although sufficiently diverse sources reported values for Cl^- and BPh_4^- that are in good agreement, so that they could be averaged and recommended, these stop at $x_{DMF} = 0.5$.

The rather low $\Delta_t G°(OH^-)$ values from Mandal et al.[67] appear to be incorrect, in view of the fact that for transfers into other many aqueous solvents these and $\Delta_t G°(Cl^-)$ have values of similar magnitude. Little can be said about the validity of the data for other anions, though the somewhat negative values for $\Delta_t G°(I^-)$ from Bhattacharya et al.[68] seem suspect.

3.17. Transfer to Aqueous *N*-Methylpyrrolidin-2-one

The available data for the Gibbs energy of transfer of anions from water into aqueous mixtures of *N*-methylpyrrolidin-2-one (NMPy), $\Delta_t G°(A^-, W \rightarrow W + NMPy)$, are shown in Table 17. For each anion, however, entries could be found from only a single source, so that no comparative evaluation of the data could be made. The exception to this, BPh_4^-, presents an even worse problem, in view of the serious discrepancies between the values reported by Gomaa[69] and Varadarajan et al.,[70] although both purport to be based on the TATB assumption that involves BPh_4^-. It is certainly not the small difference in temperature between the data from these two sources that can be responsible for the notable

Table 17. Standard Molar Gibbs Energies of Transfer of Anions from Water to *N*-Methylpyrrolidin-2-one (NMPy) + Water Mixtures at 298.15 K, $\Delta_t G°$(ion)/kJ mol^{-1}, Molarity Scale

	$\Delta_t G°$(ion)/kJ mol^{-1} at the following values of 100x_{NMPy}											
	10	20	30	40	50	60	70	80	90	100	method	ref
Cl^-	19.9	29.8	34.1	36.2	38.3	41.4	45.5			46.1	TATB	69
Br^-	13.1	19.7	22.7	24.0	24.9	26.4	28.5			30.4	TATB	69
I^-	10.8	16.0	17.7	18.1	18.4	19.3	20.9			21.8	TATB	69
BrO_3^-	7.1		12.6		18.5		28.7		31.2	40.9	TATB*	*a*
IO_3^-	4.4		5.8		10.1		17.6		18.8	28.4	TATB*	*a*
HCO_2^-	5.0	9.1	12.6	15.6	18.3	20.7	23.1	25.5	28.1	31.0	TATB*	70
$PhCO_2^-$	4.1	6.0	6.5	6.1	5.2	4.4	4.1	4.7	6.8	10.8	TATB*	70
Pic^-	−1.1	−0.7	−0.3	0.1	0.5	0.9	1.3	1.7	2.1	2.4	TATB*	70
BPh_4^-	−20.1	−29.5	−33.1	−34.2	−35.2	−37.4	−40.6			−40.1	TATB	69
	−2.4	−4.5	−6.6	−8.7	−10.8	−12.9	−15.0	−17.2	−19.3	−21.4	TATB*	70
$C_2O_4^{2-}$	7.3		10.7		18.4		33.6		38.5	56.4	TATB*	*a*
SO_4^{2-}	22.0		42.1		36.2		67.8		72.4	89.2	TATB*	*a*

*At 303.15 K. [a] Varadarajan, T. K.; Parvathy, R.; Ramakrishna, T. V.; Kalidas, C. *J. Chem. Eng. Data* **1995**, *40*, 883.

Table 18. Standard Molar Gibbs Energies of Transfer of Anions from Water to *N,N,N′,N′,N″,N″*-Hexamethylphosphoric Triamide (HMPT) + Water Mixtures at 298.15 K, $\Delta_t G°$(ion)/kJ mol^{-1}, Molarity Scale

	$\Delta_t G°$(ion)/kJ mol^{-1} at the following values of 100x_{HMPT}											
	10	20	30	40	50	60	70	80	90	100	method	ref
Cl^-	23.3	38.1	46.6	48.6	51.5	53.8	55.7	57.1	57.6	56.8	K^+, Ph_4As^+	71
Br^-	16.5	28.3	33.9	33.6	35.0	36.3	37.7	39.2	40.3	40.7	K^+, Ph_4As^+	71
I^-	14.4	22.7	26.8	25.5	25.3	27.0	28.1	29.2	29.8	29.9	K^+, Ph_4As^+	71
BPh_4^-	−23.7	−31.3	−32.6	−34.7	−35.0	−35.2	−36.4	−38.5	−39.8	−38.0	K^+, Cs^+	71

differences. It should be noted, however, that the data reported by Gomaa[69] for mixtures very dilute in NMPy ($x_{\mathrm{NMPy}} = 0.1$) already have quite large positive values for $\Delta_t G°(A^-)$ of the halides and large negative values for BPh_4^- compared with values for other anions. Also, the $\Delta_t G°(A^-)$ reach at $x_{\mathrm{NMPy}} = 0.6$ nearly 90% of the values they have for neat NMPy.[69] Such behavior is rather unusual, a fact that casts some doubt upon their validity.

3.18. Transfer to Aqueous *N,N,N′,N′,N″,N″*-Hexamethylphosphoric Triamide

The few available data for the Gibbs energy of transfer of anions from water into aqueous mixtures of *N,N,N′,N′,N″,N″*-hexamethylphosphoric triamide (HMPT), $\Delta_t G°(A^-, W \rightarrow W+HMPT)$, are shown in Table 18. As is the case with transfer into aqueous formamide, there is a single source for the data,[71] and no comparative evaluation of the data could be made. The data are, however, averages between results for two salts in each case, that are in good agreement with each other (generally within 1 kJ mol^{-1}), a fact that lends some credence to them.

3.19. Transfer to Aqueous Dimethyl Sulfoxide

Much more extensive information is available regarding the Gibbs energy of transfer of anions from water into aqueous mixtures of dimethyl sulfoxide (DMSO), $\Delta_t G°(A^-, W \rightarrow W+DMSO)$, as is shown in Table 19. In the cases of Cl^-, Br^-, I^-, and BPh_4^-, sufficient diversity of the sources of the data permits the averaging of the results and presentation of recommended sets of values. Note that the values of $\Delta_t G°(F^-)$ reported by Hefter[72] were in terms of integral kJ mol^{-1} numbers, so that the averages for the three cations (only two at each solvent composition) should not convey the impression of better precision. As far as the $\Delta_t G°(F^-)$ values from Bhattacharya et al.[73] go, they are in agreement with the former set, and it is noteworthy that the $\Delta_t G°(OH^-)$ values from Bhattacharya et al.[73] are similar to these too. The lower values for $\Delta_t G°(OH^-)$ from the other two sources appear to be inconsistent with this. The data for copper(II) iodate, acetate, and benzoate that were evaluated by Rajendran et al.[74] use the negligible liquid junction potential (NLJP) extrathermodynamic assumption rather than the TATB one. It was shown by Kundu and Parker[58] that such results can be adjusted by adding $\sim 3x_{\mathrm{DMSO}}$ kJ mol^{-1} to the cation transfer values and subtracting this quantity from the anion values to convert them to the TATB scale. However, in Table 19 the values were recalculated instead with the Cu^{2+} recommended data on the TATB scale from ref 1.

4. General Discussion of the Data

The salient feature of the data presented in all the Tables 1−19 is the division into $\Delta_t G°(A^{n-}) > 0$ for hydrophilic anions and < 0 for hydrophobic ones, with few exceptions. The hydrophobic anions for which data could be included are only picrate and tetraphenylborate; the other anions included are hydrophilic, although some are borderline cases. Exceptions are protic solvents, such as 1,2-ethanediol and glycerol, that show $\Delta_t G°(A^-) < 0$ for iodide (and also bromide for the latter) for transfer into their aqueous mixtures. The borderline cases are those that have $\Delta_t G°(A^-) < 0$ for water-rich mixtures but $\Delta_t G°(A^-) > 0$ for cosolvent-rich ones, e.g., cyanide, thiocyanate, and possibly perchlorate.

A clear gradation of transfer Gibbs energies is evident in the halide series: $\Delta_t G°(F^-) > \Delta_t G°(Cl^-) > \Delta_t G°(Br^-) > \Delta_t G°(I^-)$ for all solvent mixtures for which there are reliable data. This is shown at $x_{\mathrm{cosolvent}} = 0.2$ in Figure 1. The ordering of the solvents in Figure 1 is according to increasing $\Delta_t G°(Br^-)$ (for which data are available for all the solvents discussed in this review), but very similar trends would be seen if the order were according to increasing $\Delta_t G°(Cl^-)$ or $\Delta_t G°(I^-)$. The deviations noted from smooth curves are probably due to inaccuracies in the data, noted most clearly for $\Delta_t G°(F^-)$ transferring to dilute aqueous formamide (No. 5), *N,N*-dimethylformamide (No. 10), and dimethyl sulfoxide (No. 11) with too high values and for transfer into dilute aqueous acetonitrile (No. 8) and 2-methoxyethanol (No. 9) with too low values. Leading the solvents with low $\Delta_t G°(A^-)$

Table 19. Standard Molar Gibbs Energies of Transfer of Anions from Water to Dimethylsulfoxide (DMSO) + Water Mixtures at 298.15 K, $\Delta_t G°$(ion)/kJ mol^{-1}, Molarity Scale

	$\Delta_t G°$(ion)/kJ mol^{-1} at the following values of $100x_{DMSO}$											
	10	20	30	40	50	60	70	80	90	100	method	ref
OH^-	4.6	11.9	18.6	25.1							H^+	*a*
	10.1	19.8	31.7								K^+	73
	4.2	7.6	11.9	16.8							H^+	67
F^-	9.2	16.3	26.9								K^+	73
	9	19	30	41	48	52	57	62	68	72	Li^+, Na^+, K^+	72
Cl^-	4.7	9.8	15.5	20.9	25.0	27.1					H^+, Rb^+	37
	4.3	9.2	14.9	20.6	25.3		30.8			39.0	M^+ *	63
	4.4	9.5	15.0	20.5	24.7	27.3	29.8	32.5	35.6	38.7	M^+ *	*b*
	4.3	10.0	16.0								K^+	73
	4.2	9.0	13.9	18.7	23.4	27.9	31.8	35.3		39.9	TATB	21
	4.7	10.1	16.0	21.5	25.5	26.8					M^+ **	58
	2.6	7.6	12.3	17.4	21.5	21.8					H^+	*c*
	4.8	10.4	15.9								M^+ **	*d*
	4.7	9.8	15.4								Na^+, K^+	*e*
	4.6	10.2	15.7	21.0	25.8	28.8					see text	*f*
	4.5	**9.7**	**15.4**	**20.9**	**25.1**	**27.1**	**30.3**	{**32.5**}	{**35.6**}	**38.9**	**TATB**	**R**
Br^-	2.9	6.3	10.5	14.8	18.3		21.5			24.8	M^+ *	63
	3.2	5.8	9.6	13.1	16.6	17.8	18.9	20.4	21.9	23.9	M^+ *	*b*
	3.6	6.8	11.4								K^+	73
	2.4	7.0	11.4	16.0	19.6						H^+	58
	3.3	7.4	11.8								M^+ **	*d*
	2.8	**6.4**	**10.5**	**14.6**	**18.1**	{**17.8**}	**20.2**	{**20.4**}	{**21.9**}	**24.3**	**TATB**	**R**
I^-	0.6	2.0	4.4	7.1	9.1		10.5			12.8	M^+ *	63
	1.1	1.8	4.1	6.4	9.1	9.7	10.3	11.4	12.3	13.5	K^+	*b*
	1.5	2.6	5.1								K^+	73
	2.5	5.8	8.0	9.6	10.9	11.7	13.4	15.3	16.2	16.1	H^+	58
	1.0	2.	5.5								M^+ **	*d*
	1.5	**3.8**	**6.2**	**8.3**	**9.9**	**10.7**	**13.4**	{**15.3**}	{**16.2**}	**14.1**	**TATB**	**R**
CN^-	2.8	6.3	11.3	16.2	20.9	23.1	25.1				K^+	*f*
IO_3^-	0.7	2.4	4.4	6.7	9.8	11.3	13.4	15.0	16.1	17.0	Cu^2	74
$CH_3CO_2^-$	3.9	7.9	11.6	15.1	18.3	21.3	23.9	26.2	28.1	29.9	Cu^2	74
$PhCO_2^-$	1.0	2.9	5.1	7.4	9.8	12.1	14.1	15.8	17.0	17.9	Cu^2	74
BPh_4^-	−6.5	−13.2	−17.7	−21.4	−24.1		−31.7			−37.1	K^+, Ph_4As^+	63
	−6.9	−13.7	−18.3	−22.0	−24.5	−28.3	−32.1	−33.2	−35.0	−37.8	K^+, Ph_4As^+	*b*
	−8.5	−14.7	−20.1	−24.7	−28.5	−31.5	−33.6	−35.0	−35.5	−36.4	TATB	9
	−7.3	**−13.9**	**−18.7**	**−22.7**	**−25.3**	**−30.0**	**−32.2**	**−34.1**	**−35.3**	**−37.1**	**TATB**	**R**

*Averages of using Li^+, Na^+, K^+, Rb^+, Cs^+, and Ag^+ for Cl^-; Na^+, K^+, and Ag^+ for Br^- and I^- from ref 1. **Average of using Li^+, Na^+, K^+, Rb^+, Cs^+, and H^+ from ref 1. [a] Gillet, H.; Avedikian, L.; Morel, J.-P. *Can. J. Chem.* **1975**, *53*, 455. [b] Cox, B. G.; Waghorne, W. E. *Chem. Soc. Rev.* **1980**, *9*, 381. [c] Elsemongy, M. M.; Kennawy, I. M. *Z. Phys. Chem. (NF)* **1982**, *130*, 37. [d] Elsemongy, M. M.; Reicha, F. M. *Thermochim. Acta* **1986**, *108*, 115. [e] Egorov, G. I.; Korolev, V. P.; Krestov, G. A. *Elektrokhimiya* **1996**, *32*, 1169; *Russ. J. Electrochem.* **1996**, *32*, 1080. [f] Blandamer, M. J.; Burgess, J.; Duffield, A. J. *J. Chem. Soc., Dalton Trans.* **1980**, 1.

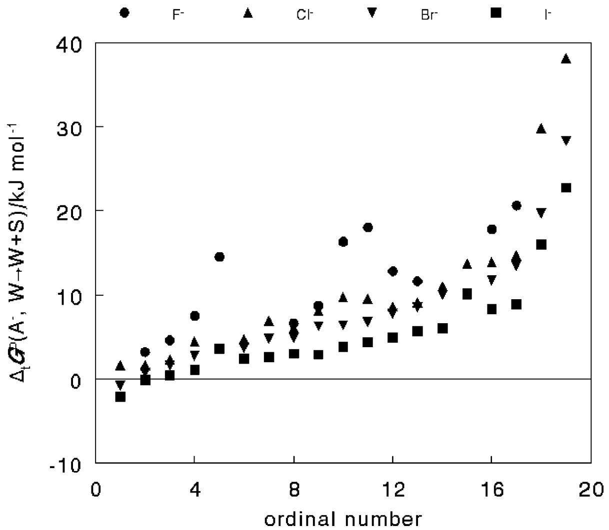

Figure 1. $\Delta_t G°(A^-, W \rightarrow W+S)$ at $x_S = 0.2$ (S = cosolvent) for $A^- = F^-$, Cl^-, Br^-, and I^-, ordered according to increasing values of $\Delta_t G°(Br^-)$. The ordinal numbers of S pertain to (1) Gly, (2) MeOH, (3) EG, (4) EtOH, (5) FA, (6) PG, (7) 2-PrOH, (8) MeCN, (9) 2-MeOEtOH, (10) DMSO, (11) DMF, (12) EC, (13) *t*-BuOH, (14) Diox, (15) THF, (16) Me_2CO, (17) DME, (18) NMPy, and (19) HMPT (for the abbreviations of the cosolvent names, consult the text).

values are those with good hydrogen bond donating properties, alkan(tri, di, mono)ols and formamide. Closing the list of solvents are those aprotic dipolar ones, for which the positive end of their dipoles is deeply imbedded in the molecules, NMPy and HMPT, hindering access by the anions. The latter solvents tend to bind the water molecules in the aqueous mixture by hydrogen bonding to the more exposed negative ends of the dipoles, making the water molecules less able to solvate the anions. Thus, the hydrogen bond accepting propensities of the halide anions and the hydrogen bond donating and accepting abilities of the aqueous solvents are the factors responsible for the anions leaving the water and entering the environment in the water + cosolvent mixtures.

Further series of $\Delta_t G°(A^-)$ values, but with much fewer data available, are the halates, with none being sufficiently confirmed to warrant recommendation, but average values could be derived from the data. Here, the values at $x_S = 0.1$ are shown in Figure 2, ordered according to increasing values of $\Delta_t G°(IO_3^-)$, with the gradation $\Delta_t G°(IO_3^-) > \Delta_t G°(BrO_3^-) > \Delta_t G°(ClO_3^-)$ being seen. Out of order are the values for bromate and iodate for transfer into aqueous *N*-methylpyrrolidin-2-one, for no obvious reason. The gradation established for these dipolar anions is explained in a similar manner as for the halides, noting that the ability of being hydrated is largest for iodate. The trigonal pyramidal structure of IO_3^- is the "flattest" of the three halates, permitting most ready access of the hydrogen bond donating water molecules to the negative end of the anion dipole. The order among

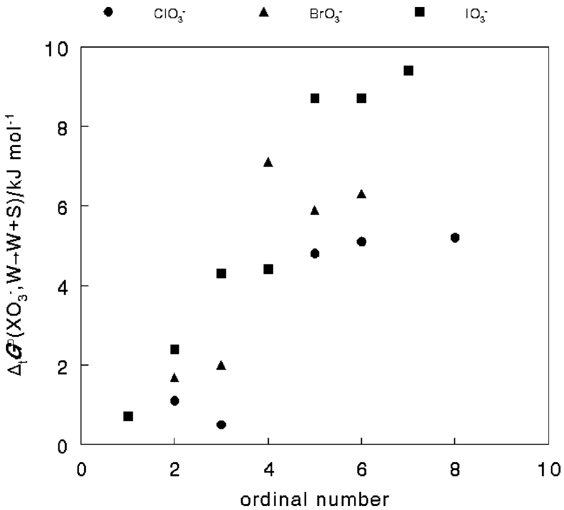

Figure 2. $\Delta_tG°(XO_3^-,W\rightarrow W+S)$ at $x_S = 0.1$ (S = cosolvent) for X = Cl, Br, and I, ordered according to increasing values of $\Delta_tG°(IO_3^-)$. The ordinal numbers of S pertain to (1) DMSO, (2) MeOH, (3) MeCN, (4) NMPy, (5) 2-PrOH, (6) *t*-BuOH, (7) DMF, and (8) Me_2CO (for the abbreviations of the cosolvent names, consult the text).

the cosolvents is less clear, inasmuch as very dilute mixtures of the cosolvent in water are involved, so that solvent−water interactions overshadow the solvent−anion ones.

Very few data on the Gibbs energy of transfer of multivalent anions from water into aqueous mixtures with cosolvents have been published. It is expected that such anions are more hydrophilic than univalent ones and should invariably have positive $\Delta_tG°(A^{n-})$ values, as is generally the case. Still, there are a few cases in which the anions appear to prefer the mixed solvent in water-rich mixtures. If the data for such cases are accepted as true (but see the text accompanying the tables), they can be explained as follows. These cases involve large anions that disrupt the water structure strongly and prefer a less structured environment that can still provide hydrogen bonds for their solvation. Instances that have been reported are $Cr_2O_7^{2-}$ and $Fe(CN)_6^{3-}$ in aqueous methanol and WO_4^{2-} in aqueous dioxane, but no independent confirmation of these negative $\Delta_tG°(A^{n-})$ values has been provided, and their validity may be doubted.

The Gibbs energies of transfer of both cations and anions $I^{\pm}$ need to conform to the expression

$$\Delta_tG°(I^{\pm}) = \Delta_tH°(I^{\pm}) - T\Delta_tS°(I^{\pm}) \qquad (8)$$

and agree with the values of $\Delta_tH°(I^{\pm})$ and $\Delta_tS°(I^{\pm})$ selected previously as reliable by Hefter, Marcus, and Waghorne.[75] They generally do conform within the probable errors of each of these quantities. However, due to the enthalpy−entropy compensation noted for many transfer systems, but mainly for cations, the $\Delta_tG°(I^{\pm})$ would be small differences between considerably larger values. Hence, it is inadvisable to try to obtain unavailable $\Delta_tG°(I^{\pm})$ from the recommended enthalpy and entropy data.[75] On the other hand, a combination of the recommended $\Delta_tG°(A^-)$ values in the present review and $\Delta_tH°(A^-)$ from the previous one[75] may provide $\Delta_tS°(A^-)$ data missing in the latter. Such data are shown in Table 20, as rounded values from curve-fits to $[\Delta_tH°(A^-) - \Delta_tG°(A^-)]/T$ values, with probable errors of ±3 J K^{-1} mol^{-1}.

Table 20. Standard Molar Enntropies of Transfer of Anions from Water to C-Solvent (S) + Water Mixtures at 298.15 K, $\Delta_tS°$(ion)/J K^{-1} mol^{-1}, Molarity Scale, Derived from $\Delta_tS° = (\Delta_tH° - \Delta_tG°)/T$, with $\Delta_tH°$ from Ref 161 and $\Delta_tG°$ from the Reference Shown

	$\Delta_tS°$(ion)/J K^{-1} mol^{-1} at the following values of 100x_s											
anion	5	10	20	30	40	50	60	70	80	90	100	ref
					S = MeOH							
SCN$^-$	6	6	−3	−14	−21	−21	−17	−11	−6	−6	−6	R
NO$_3^-$	5	6−2	−15	−22								33
					S = EtOH							
OH$^-$	−12	−23	−36	−39								*a*
F$^-$	−5	−9	−13	−16	−19	−22	−26	−27	−24			*b*
NO$_3^-$	−5	−10	−19	−28	−35							*a*
ClO$_4^-$	9	7	−9	−22	−25	−24	−28	−37	−37			*a*
					S = EG							
F$^-$	−2	−1										T
					S = Gly							
Br$^-$	8	14	16*									45
I$^-$	10	16	17*									45
Pic$^-$	4	8	14*									*c*
					S = MeCN							
SCN$^-$							−102	−120	−137	−154	−170	*d*
BrO$_3^-$	−3	0	8	4	−12	−20						*e*
					S = FA							
F$^-$	−14	−24	−34	−39	−44	−50	−57	−59	−50			66
Br$^-$		−22	−23									65
I$^-$	−18	−29	−34	−31	−28	−29	−33	−38	−40	−40	−40	65
					S = DMF							
F$^-$	−32	−53	−74	−79								73
					S = HMPT							
Cl$^-$	9	8	−13	−40								71
Br$^-$	11	16	13	2	−9	−17	−24	−31	−40	−49	−56	71
I$^-$	−7	−16	−37	−56	−71	−83	−96	−110	−126	−138	−136	71
					S = DMSO							
OH$^-$	−30	−38	−18	−8								73

*At $x_S = 0.15$. [a] Blandamer, M. J.; Briggs, B.; Burgess, J.; Elvidge, D.; Guardado, P.; Hakin, A. W.; Radulovich, S.; Hubbard, C. D. *J. Chem. Soc., Faraday Trans. 1* **1988**, *84*, 2703. [b] Senanayake, G.; Hefter, G. *Monatsh. Chem.* **2003**, *134*, 669. [c] Talukdar, H.; Rudra, S.; Kundu, K. K. *Can. J. Chem.* **1989**, *67*, 321. [d] Giridhar, V. V.; Kalidas, C. *J. Solution Chem.* **1982**, *11*, 539. [e] Subramanian, S.; Rao, S. C. A. V. S. S.; Kalidas, C. *Indian J. Chem. A* **1981**, *A20*, 723.

As a general conclusion, it may be stated that the present review may be consulted in conjunction with that on the cations[1] and with the review on the standard molar enthalpies and entropies of transfer, $\Delta_tH°(I^{\pm})$ and $\Delta_tS°(I^{\pm})$,[75] in order to gain more insight into the solvation properties of the ions in aqueous−cosolvent mixtures. If data on the transfer of electrolytes to aqueous−organic solvent mixtures that have not been studied directly are needed, they can be reconstructed from the values for the individual cations and anions. An instance of the application of such considerations is the ability to obtain a rough indication of the solubilities of electrolytes (their solubility products, K_{sp}) in such solvent mixtures from the use of eq 2.

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