918. *Studies in Ion Solvation in Non-aqueous Solvents and their Aqueous Mixtures. Part III.*[1] *The Cell* $H_2|HX|AgX{-}Ag$ ($X = Br$ *or* I) *in* 20 *and* 45% *Mixtures of Dioxan and Water at* 25°

By D. Feakins and D. J. Turner

Standard e.m.f. values at 25° for the cells $H_2|HX|AgX{-}Ag$ ($X = Br$ or I) in 20 and 45% mixtures of dioxan with water are reported. Molar free energies of transfer from water to the mixtures are calculated for the pairs of ions H^+Cl^-, H^+Br^-, H^+I^-, and H^+OH^-, and separated into individual ionic values by the method of Part II.[1] The pattern of these values is qualitatively similar to that for transfers from water to methanol–water mixtures.[1] The hydroxide ion has the properties expected of a spherically symmetrical ion of radius 1·53 Å.

In this Paper we describe the determination, and discuss the significance, of the standard e.m.f. values ($E°$) at 25°, of the cells

$$H_2|HBr|AgBr{-}Ag \qquad (I)$$

and

$$H_2|HI|AgI{-}Ag \qquad (II)$$

in dioxan–water mixtures. (Cell numbers are, where possible, the same as in Part I.[2]) Mixtures containing 20 and 45% of dioxan by weight were chosen to give results comparable with those found[3] using the cell

$$H_2|HCl|AgCl{-}Ag \qquad (V)$$

at the same concentrations of dioxan.

It was first found that the hydrogen electrodes behaved reversibly in solutions containing

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[1] Part II, D. Feakins and P. Watson, *J.*, 1963, 4734.
[2] D. Feakins and P. Watson, *J.*, 1963, 4686.
[3] H. S. Harned, *J. Amer. Chem. Soc.*, 1938, **60**, 336.

dioxan only if it had been rigorously freed from peroxides. Thus, even purified dioxan, initially free from peroxides, was unsuitable after about a week of storage under nitrogen.

A method[4] in which this "stock" dioxan was passed through a column of alkali-free activated alumina before use gave a peroxide-free product. However, tests using cell V revealed that impurities were eluted from the column, and the method was abandoned in favour of one in which a sample of "stock" dioxan which had been kept over sodium was freshly redistilled from sodium, in an atmosphere of nitrogen, for each measurement. A peroxide-free product, in whose aqueous solutions the hydrogen electrodes were highly reversible, was again obtained, and the literature e.m.f. values of cell V could be closely reproduced if it was used to make a 20% dioxan–water mixture. Any oxidation of this material was minimised by making cell solutions with nitrogen-saturated conductivity water, saturating them immediately after preparation with hydrogen, and thereafter keeping them in an atmosphere of hydrogen or nitrogen.

Owen's[5] method, in which oxidation of the iodide ion is inhibited by buffering the cell solutions to high pH, was chosen to determine the E° values. The E° values of cell V being known, this method involves measurements on two more cells:

$$H_2|HBO_2(m)NaBO_2(m)KCl(m)|AgCl\text{–}Ag \qquad \text{(III)}$$

and

$$H_2|HBO_2(m)NaBO_2(m)KI(m)|AgI\text{–}Ag \qquad \text{(IV)}$$

We first attempted to obtain the standard e.m.f. of cell I directly, using hydrobromic acid as the electrolyte, because this procedure had worked satisfactorily with methanol–water mixtures as solvents.[2] With dioxan–water mixtures, the behaviour of this cell was highly reversible, and equilibrium was rapidly reached, but its e.m.f. at equilibrium could not be reproduced to better than 1—2 mv in separate runs. The dioxan was known, from the work described above, to be capable of giving reproducible results, and the hydrobromic acid was similarly tested, and found to be satisfactory, in aqueous solution in cell I. Thus, the irreproducibility of the cell could only be attributed to a reaction between dioxan and hydrobromic acid, probably one in which small, variable amounts of hydrobromic acid are consumed. This reaction could not be identified under our experimental conditions. A ring-opening reaction between the anhydrous components, which consumes hydrogen bromide, has been reported.[6]

The e.m.f. values of cell I in dioxan–water mixtures were, however, highly reproducible if the cell solutions were buffered with the borate buffers. The E° value of cell I was therefore also obtained by Owen's method. This requires measurements on cell VI as well as on cell III.

$$H_2|HBO_2(m)NaBO_2(m)KBr(m)|AgBr\text{–}Ag \qquad \text{(VI)}$$

EXPERIMENTAL

Measurements of e.m.f. were made with a Pye precision vernier potentiometer in conjunction with a sensitive galvanometer and a standard cell.

The simple experimental cell used previously[2] did not give e.m.f. values of adequate temporal stability with the dioxan–water systems. In the modified cell, hydrogen and silver–silver halide compartments were connected by a cross-piece containing a tap which was partially opened for measurements of e.m.f. but otherwise kept closed. Hydrogen was delivered to the hydrogen electrode compartment and nitrogen to the silver–silver halide compartment through two pre-saturators in series in each case; it escaped through long capillary tubes. Two electrodes for each compartment were mounted on a standard Pyrex through-cone. By using Pyrex–soda-glass graded seals, the platinum-to-glass seals could be made with soda glass.

For a measurement, the solution was saturated with hydrogen and forced into the cell and

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[4] W. Dasler and C. D. Bauer, *Ind. Eng. Chem., Analyt.*, 1946, **18**, 52.

[5] B. B. Owen, *J. Amer. Chem. Soc.*, 1935, **57**, 1526.

[6] A. B. Van Cleave and R. I. Blake, *Canad. J. Chem.*, 1951, **29**, 785.

saturators under a pressure of hydrogen, using an all-glass gas line. The cell assembly was transferred to a water-bath kept at 25° ± 0·01° and nitrogen and hydrogen passed through their respective stoppered compartments for 30 min. before introduction of the electrodes in place of the stoppers. Only diffused light fell on the halide electrodes. The bias e.m.f. of two electrodes in the same compartment was rarely more than 5 μv for the halide electrodes, and normally less than 1 μv for the hydrogen electrodes. When the cell was at equilibrium (e.m.f. constant to ±0·01 and ±0·02 mv for the 20 and 45% mixtures, respectively, for at least 2 hr.), the e.m.f. was recorded as the mean of those between the four combinations of electrodes in the cell. Equilibration times were from 1 to 1½ hr., the halide electrodes having been "aged" previously. Hydrogen electrodes were made by Hills and Ives's method.[7] Only two changes were made in the preparation of silver–silver halide electrodes previously described.[2] First, in the pyrolysis of the silver oxide paste, it was brought slowly to 500° and left there for 10 min. Secondly, the electrodes were kept in conductivity water following their preparation, and, after an ageing period, which was longest (up to 2 days) for the iodide electrodes, they could be used for several measurements, retaining their low bias e.m.f.s and generally reversible behaviour for up to 2 months.

Hydrobromic acid, potassium iodide, borax, and conductivity water were as before.[2] ($Na_2B_4O_7$ made by heating borax at 800° for 4 hr. dissolved inconveniently slowly in dioxan–water mixtures.) AnalaR potassium chloride was recrystallised six times from conductivity water (it was then free from bromide ions; uranine test [8]), dried at 110°, and kept in a desiccator over silica gel. AnalaR potassium bromide was recrystallised four times from conductivity water, dried at 110°, and stored in a desiccator over silica gel. Dioxan (May and Baker) (2 l.) was refluxed (12 hr.) with concentrated hydrochloric acid (25 ml.) and distilled water (200 ml.), a slow stream of nitrogen being passed through the mixture. Excess of potassium hydroxide was added. The upper layer of dioxan was decanted, allowed to stand (24 hr.) over fresh potassium hydroxide, decanted, refluxed (12 hr.) over freshly cut sodium in an atmosphere of nitrogen, and distilled from the sodium through an electrically heated 4-ft. column packed with Fenske helices. The fraction boiling in the range 101·2—101·4° was collected.[9] It had f. p. 11·76—11·78° (lit.,[10] 11·76—11·80°). This "stock" dioxan was stored over sodium in an atmosphere of nitrogen, and redistilled freshly through a similar fractionating column.

DISCUSSION

If E_{HCl} and E_{HI} are, respectively, the e.m.f.s of cells III and IV at the same value of m, with $E^{\circ}_{\text{m,HCl}}$ and $E^{\circ}_{\text{m,HI}}$ the corresponding standard molal e.m.f.s, and if, in general, γ_{Y} denotes the molal activity coefficient of the species Y, then, with $k = 2{\cdot}3026\boldsymbol{RT}/\boldsymbol{F}$, it can be shown [2] that

$$E^{\circ}_{\text{m,HI}} = E^{\circ}_{\text{m,HCl}} + E_{\text{HI}} - E_{\text{HCl}} - k \log (\gamma_{\text{Cl}}/\gamma_{\text{I}}). \tag{1}$$

Log $(\gamma_{\text{Cl}}/\gamma_{\text{I}})$ is small if m is $\leqslant 0{\cdot}01$. If it is linear in m,[2] we may put

$$E^{\circ\prime}_{\text{m,HI}} = E^{\circ}_{\text{m,HI}} + \lambda_1 m, \tag{2}$$

where

$$E^{\circ\prime}_{\text{m,HI}} = E^{\circ}_{\text{m,HCl}} + E_{\text{HI}} - E_{\text{HCl}} \tag{3}$$

and λ_1 is an empirical constant. $E^{\circ}_{\text{m,HI}}$ can, in principle, be found by plotting a graph of $E^{\circ\prime}_{\text{m,HI}}$ against m and extrapolating to $m = 0$. The e.m.f.s of cells III and VI may be treated similarly, to give $E^{\circ}_{\text{m,HBr}}$, the molal standard e.m.f. of cell VI.

This procedure was followed to give $E^{\circ}_{\text{m,HBr}}$ and $E^{\circ}_{\text{m,HI}}$ in the 20% dioxan–water mixture. In the case of the 45% mixture, the results were slightly less accurate, covered only a very small range of ionic strength, and showed no clear trend with m outside the

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[7] G. J. Hills and D. J. G. Ives, *J.*, 1951, 305.

[8] G. D. Pinching and R. G. Bates, *J. Res. Nat. Bur. Stand.*, 1946, **37**, 311.

[9] K. Hess and H. Frahm, *Ber.*, 1938, **71**, 2627.

[10] J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier, New York, 1950, p. 502.

experimental error. Extrapolation according to equation (2) did not therefore appear to be justified, and the E°_{m} values recorded are averages of the $E^{\circ\prime}_{m}$ values. Values of E_{HCl}, E_{HBr}, E_{HI}, $E^{\circ\prime}_{m,HBr}$, and $E^{\circ\prime}_{m,HI}$, at various values of m are shown in Table 1.

TABLE 1

m	E_{HCl} (v)	E_{HBr} (v)	E_{HI} (v)	$E^{\circ\prime}_{m,HBr}$ (v)	$E^{\circ\prime}_{m,HI}$ (v)	pK'
			20% *Dioxan*			
0·0040	0·93879	0·79557	0·58431	0·05981	−0·15145	10·045
0·0045	0·93592	0·79271	0·58136	0·05982	−0·15153	10·046
0·0050	0·93323	0·79001	0·57885	0·05981	−0·15135	10·047
0·0055	0·93077	0·78758	0·57623	0·05984	−0·15151	10·046
0·0060	0·92858	0·78538	0·57402	0·05983	−0·15153	10·047
0·0070	0·92464	0·78131	0·57011	0·05970	−0·15150	10·046
0·0075	0·92294	0·77965	0·56820	0·05974	−0·15170	10·048
0·0080	0·92129	0·77800	0·56663	0·05974	−0·15163	10·047
0·0085	0·91970	0·77642	0·56504	0·05975	−0·15163	10·047
0·0090	0·91829	0·77498	0·56363	0·05972	−0·15163	10·048
0·0115	0·91197	0·76860	0·55726	0·05966	−0·15168	10·047
			45% *Dioxan*			
0·0060	0·96837	0·83664	0·64484	0·03185	−0·15994	11·389
0·0070	0·96428	0·83258	0·64054	0·03188	−0·16022	11·385
0·0075	0·96255	0·83072	0·63856	0·03172	−0·16041	11·386
0·0080	0·96079	0·82908	0·63682	0·03185	−0·16039	11·383
0·0090	0·95780	0·82605	0·63392	0·03183	−0·16030	11·383

The method essentially measures $E^{\circ}_{m,HCl} - E^{\circ}_{m,HX}$. The errors on this quantity are, for 20% dioxan, in both cases, ±0·05 mv, and for 45% dioxan, ±0·07 mv for X = Br and ±0·17 mv for X = I. Adding the errors on $E^{\circ}_{m,HCl}$, which are somewhat difficult to assess, $E^{\circ}_{m,HBr}$ is known to about ±0·1 mv in both the 20 and the 45% mixture, the corresponding values for $E^{\circ}_{m,HI}$ being ±0·1 and ±0·2 mv. The E°_{m} values are in Table 2.

TABLE 2

E°_{m} for cells $H_2|HX|AgX\text{–}Ag$, in volts

Solvent	HCl	HBr	HI
Water (for sources see ref. 2)	0·2224	0·0712	−0·15225
20% Dioxan	0·20303 (ref. 3)	0·05991	−0·15136
45% Dioxan	0·16358 (ref. 3)	0·03183	−0·16025

It can be shown [2] that, for cell III,

$$(E_{HCl} - E^{\circ}_{m,HCl})/k + \log(m_{HA}m/m_{A}) = pK - \log(\gamma_{HA}\gamma_{Cl}/\gamma_{A}) \qquad (4)$$

K is the dissociation constant of boric acid ($A = BO_2$). The ratio $m_{HA} : m_{A}$ can be corrected for hydrolysis [2] with some precision, as the ionic products of water in these mixtures are accurately known.[11] Putting the left-hand side of equation (10) equal to pK', and noting that the term in the activity coefficients should be linear in m,[2] we have

$$pK' = pK - \lambda_2 m \qquad (5)$$

Values of pK' at various values of m, obtained from measurements on cell III, are shown in Table 1. The values of pK for the two solvent mixtures, obtained by use of equation (5), are given in Table 3. They are accurate, in the case of the 20% dioxan value, to ±0·001, and in that of the 45% dioxan value to ±0·002 pK unit.

TABLE 3

Solvent	Water *	20% Dioxan	45% Dioxan
pK	9·234	10·045	11·406

* G. G. Manov, N. J. DeLollis, and S. F. Acree, *J. Res. Nat. Bur. Stand.*, 1944, **33**, 287.

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[11] H. S. Harned and L. D. Fallon, *J. Amer. Chem. Soc.*, 1939, **61**, 2374.

The values of the vapour pressures and densities of the two mixtures required in calculations are those given by Harned.[3]

In Part II,[1] it was shown that the molar free energies of transfer, ΔG_t°, of the pairs of ions H^+Cl^-, H^+Br^-, and H^+I^-, from water to 10 and 43·12% methanol–water mixtures, are approximately linear in the reciprocals of the anionic radii, r_a. By assuming, for transfers from water to a given mixture, that

$$\Delta G_t^\circ = \Delta G_t^\circ(H^+) + ar_a^{-1} \tag{6}$$

a set of individual ionic values of ΔG_t° was obtained. The value of a is some ten times that expected from the Born equation. ΔG_t° values for $Li^+Cl,^-$ Na^+Cl^-, and K^+Cl^- are approximately linear in the reciprocals of the cationic radii, r_c. By assuming that

$$\Delta G_t^\circ = \Delta G_t^\circ(Cl^-) - br_c^{-1} \tag{7}$$

a second set of individual ionic ΔG_t° values was obtained, in good agreement with the first. The sign of b is opposite to that predicted from the Born equation.

These ΔG_t° values are positive for anions, and negative, and numerically smaller, for cations. It was suggested that the methanol and water molecules in a methanol–water mixture are better electron-donors (more basic) and poorer proton-donors (less acidic) than water molecules in pure water. Thus, relative to water, the interactions in the primary solvation sheath of an ion tend to lower the cationic and raise the anionic free energies in the mixtures, explaining the specific signs of the ΔG_t° values. Methanol has a lower dipole moment than water, and its aqueous mixtures have lower dielectric constants (Table 4); therefore, the more general interactions in subsequent shells lower ΔG_t° numerically for cations and raise it for anions.

TABLE 4

Dielectric constant

Water *	Methanol–water †		Dioxan–water ‡	
	10%	43·12%	20%	45%
78·54	74·18	59·40	60·79	38·48

* J. Wyman and E. N. Ingalls, *J. Amer. Chem. Soc.*, 1938, **60**, 1182. † See ref. 2. ‡ G. Åkerlöf, *J. Amer. Chem. Soc.*, 1932, **54**, 4125.

The values of ΔG_t° for transfers of H^+OH^-, H^+Cl^-, H^+Br^-, and H^+I^- from water to 20 and 45% dioxan–water mixtures (Table 5) are positive, as expected from the Born equation, except for that of H^+I^- to the 20% mixture. The data for H^+OH^- can be unambiguously computed from the equilibrium constants for the ionisation of water in pure water and in the mixtures,[11] and the activities of water therein.[12]

If ΔG_t° is plotted against r_a^{-1} for the transfers of H^+Cl^-, H^+Br^-, and H^+I^- from water to (a) 20% and (b) 45% dioxan–water mixtures, the mean deviations from the best straight lines are (a) 8 cal. and (b) 40 cal., respectively, of the order of, and rather greater than, the experimental error. Curves passing through all three points would in both cases be slightly concave towards the axis of r_a^{-1}. The slopes of the lines are (a) $5{\cdot}05 \times 10^3$ cal. A° and (b) $1{\cdot}27 \times 10^4$ cal. A°. The slopes expected from the Born equation are (a) $6{\cdot}17 \times 10^2$ cal. A° and (b) $2{\cdot}20 \times 10^3$ cal. A°, and are incorrect by factors of 8 and 5, respectively. The

TABLE 5

ΔG_t° (cal.) molar scale

Water to	H^+OH^-	H^+Cl^-	H^+Br^-	H^+I^-
20% Dioxan	824	427	241	−40
45% Dioxan	2305	1316	867	144
r_a	1·53	1·806	1·951	2·168

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[12] A. L. Bacarella, A. Finch, and E. Grunwald, *J. Phys. Chem.*, 1956, **60**, 573.

values of $\Delta G_t^\circ(H^+)$ obtained by extrapolation to $r_a^{-1} = 0$, according to equation (6) ("extrapolation 1"), are (a) —2400 cal. and (b) —5700 cal., which generate the values of ΔG_t° for single ions in Table 6. No data for the alkali chlorides are available, and so these values cannot yet be supported by a second set based on equation (7). They should not, however, be seriously in error because they are entirely consistent, first, with the general theory of Part II, and secondly with results[13] for 50% dioxan–water mixtures. Equation (6) is further supported by the ΔG_t° values of H^+OH^-, discussed later.

TABLE 6

Values of ΔG_t° (cal.) for single ions on the molar scale

Water to	H^+	OH^-	Cl^-	Br^-	I^-
	Extrapolation 1				
20% Dioxan	−2400	3200	2800	2600	2300
45% Dioxan	−5700	8000	7000	6600	5800
Water to	*Extrapolation* 3				
20% Dioxan	−1900	2700	2300	2100	1900
45% Dioxan	−4300	6600	5600	5200	4400

The single-ion values in Table 6 show a pattern similar to that found for the methanol–water system. The dioxan molecule is more "basic" than the water molecule, and, like the methanol molecule, enhances the "basicity" of water molecules to which it is bonded.[1] It has no "acidic" function, but lowers the "acidity" of water molecules to which it is bonded. It has a lower dipole moment than water, and dioxan–water mixtures have dielectric constants lower than that of water. Thus, the energetic consequences of both primary and secondary solvation should be qualitatively similar in the two solvent mixtures.

In Table 7, the $\Delta G_t^\circ(H^+)$ values for dioxan–water are compared with the values for methanol–water mixtures, obtained by use of equation (6) only, at the same mole fraction or volume fraction of water. In whatever way the comparison is made, the proton is in much lower free-energy states in the dioxan–water mixtures despite the energetic consequences of the effect of their lower polarity upon the secondary solvation. On average, then, the molecules in a dioxan–water mixture must be stronger proton-acceptors than those in comparable methanol–water mixtures. It is likely that they are also poorer proton-donors, but this cannot be inferred with certainty from the anionic ΔG_t° values.

TABLE 7

$\Delta G_t^\circ(H^+)$ (cal.), molar scale, for transfers to the dioxan–water mixtures and to methanol–water mixtures of (α) the same volume fractions and (β) the same mole fraction

	Methanol–water	
Water to dioxan–water	α	β
−2400	−800	−480
−5700	−2500	−1230

As the dioxan content of the mixture increases, from 20 to 45%, and therefore the probability of finding dioxan molecules in the primary solvation sheaths of the ions also increases, the ratio of the value of *a* [equation (6)] to that expected from the Born equation falls from about 8 to about 5. Further, both ratios are lower than those found for comparable methanol–water mixtures (about 11). The strong specific interactions possible between an anion and the hydrogen atoms of water or methanol molecules are absent between the ion and dioxan molecules, and the Born equation may be expected to fit increasingly better as the dioxan content of the mixture is increased.

In the Figure, the free energies of transfer of H^+OH^- from water to the two dioxan–water mixtures are included in the graphs of ΔG_t° against r_a^{-1}. The value of 1·53 Å

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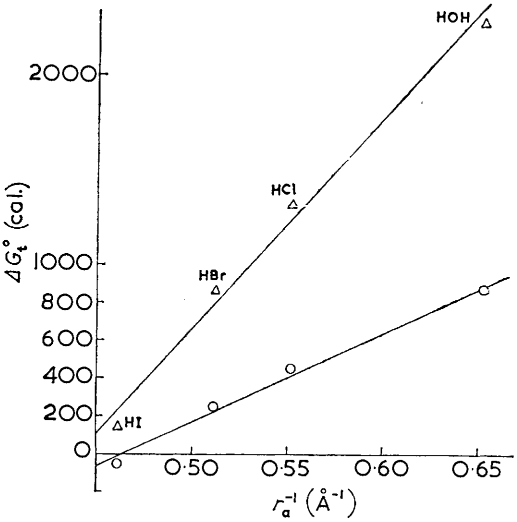
[13] E. Grunwald, G. Baughman, and G. Kohnstam, *J. Amer. Chem. Soc.*, 1960, **82**, 5801.

used for the radius of the hydroxide ion is that found in crystals wherein the ion behaves as though it were spherically symmetrical.[14] In both cases quite good straight lines are obtained, from which the mean deviations are (a) 25 cal. and (b) 68 cal., rather greater than for the halogen acids alone. $\Delta G_t°(H^+)$ from equation (6) ("extrapolation 2") becomes (a) —2100 cal. and (b) —4900 cal. If the points for H^+I^- are omitted the mean deviations become (a) 7 cal. and (b) 13 cal., the latter indicating the best fit to equation (6) for transfer (b) so far. $\Delta G_t°(H^+)$ becomes for (a) —1900 cal. and for (b) —4300 cal. ("extrapolation 3").

To explain the behaviour of the hydroxide ion, suppose, for simplicity, that the change, Δq, on going from a water molecule in pure water to a water or a dioxan molecule in a dioxan–water mixture, in the formal charges in the oxygen lone-pair orbitals and on the hydrogen atoms of a water molecule, is the same in all cases. All become more negative, *i.e.*, Δq is negative.

If a halide ion is assumed to be surrounded by four water molecules, each having a hydrogen atom adjacent to a tetrahedrally disposed lone-pair orbital, then the leading term in the expression for $\Delta G_t°$ will be proportional to $-4\Delta q(e/r)$, where e is the protonic charge, r the ionic radius, and (e/r) therefore the electric potential at the surface of the ion.



Water to dioxan–water transfers for HOH, HCl, HBr, and HI
O 20% by weight of dioxan;
Δ 45% by weight of dioxan

Let us suppose that a tetrahedral disposition of charge is also found in the hydroxide ion,[15] with the difference that a total negative charge of, say, $-(1 + x)e$, is concentrated into the three lone-pair orbitals and a charge of xe in the O–H bond orbital. The potential at the surface of the ion is, over the negative part, $-(4/3r)(1 + x)e$, and, over the positive part, $+4xe/r$. Three water molecules are orientated with a hydrogen atom adjacent to the lone-pair orbitals. A fourth, or a dioxan molecule, is orientated with an oxygen lone-pair orbital collinear with the O–H bond. The leading term in $\Delta G_t°$ is now proportional to

$$(4xe/r)\Delta q - (4/3r)(1 + x)e.3\Delta q$$

or $-4\Delta q(e/r)$ as before. To solvent molecules in subsequent sheaths the ionic charge distribution will appear to be spherically symmetrical, and the secondary solvation will be the same as for a monatomic ion of the same radius and charge. Though it is unlikely

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[14] A. F. Wells, "Structural Inorganic Chemistry," Oxford University Press, Oxford, 2nd edn., 1950, p. 414.

[15] J. D. Bernal and H. D. Megaw, *Proc. Roy. Soc.*, 1955, *A*, **151**, 384.

that Δq will be the same in all the cases mentioned above, the effect of any difference will be small if x is small.

The points for H^+I^- deviate from the straight lines joining those for H^+OH^-, H^+Cl^-, and H^+Br^- in the sense that their free-energies of transfer are less than those expected if the interactions of the ion with the solvent were simply those of a rigid charged sphere. Designating these interactions, "ionic," we may refer to any other interactions as "non-electrolytic."

In Part II, it was suggested that the "non-electrolytic" contributions to $\Delta G_t°$ could be especially important for halide ions. These contributions are likely to favour the transfer of all ions from water to aqueous or pure organic solvents, just as the transfer of the Group 0 gases to organic solvents is favoured.*

The curvature of the plots of $\Delta G_t°$ against r_a^{-1}, observed both in this work and previously, is in the sense expected if the numerical magnitude of this effect, which, if it were analogous to the effect found for Group 0 gases, would be such as to favour the transfer of a large ion with respect to a smaller one, increased rapidly as r_a increased. The inclusion of the value for H^+OH^- in the plots of $\Delta G_t°$ against r_a^{-1} shortens the extrapolation which gives $\Delta G_t°(H^+)$, and, by including data for a smaller ion, reduces the effect of the non-electrolytic contribution. It is significant that the omission of the values for H^+I^- results in the best fits to equation (6). We tentatively suggest that the "non-electrolytic" contribution to $\Delta G_t°(I^-)$ is particularly important. The sets of single-ion values based on the values of $\Delta G_t°(H^+)$ obtained from the last extrapolation (Table 6) are thought to be the most probable ones.

The iodide ion is also anomalous in that $\Delta G_t°$ for H^+I^- does not increase monotonically with increase in dioxan content, but at first decreases. Its behaviour in this respect is similar in methanol–water mixtures,[16] and is in contrast to that of the alkali chlorides and the other halogen acids.[1]

In Part II,[1] it was stated that the method of determining individual ionic values of $\Delta G_t°$ was only semi-quantitative, and it was not claimed that the correct dependence of $\Delta G_t°$ upon r had been established. de Ligny and Alfenaar [17] recently tried to refine the method, and, among other things, to allow quantitatively for the non-electrolytic interactions. This was done by identifying the non-electrolytic part of $\Delta G_t°$ for a particular ion with the value which would be expected for an "inert" species of the same radius, interpolated from graphs of $\Delta G_t°$ against r^2 for the Group 0 gases and methane. Although such considerations may be useful in semi-quantitative discussion, as here and in Part II,[1] their quantitative validity is doubtful. The dispersion forces are functions of atomic parameters, *e.g.*, the polarisability, which are markedly different for an anion, a cation, and an inert-gas atom of the same radius.

The linear variation of $\Delta G_t°$ of the "inert" species with the mole fractional composition of the methanol–water mixtures, assumed by these authors in the absence of the necessary experimental data, is also of doubtful validity in view of recent work showing that the free-energy of transfer of argon from water to ethanol–water mixtures is by no means linear in the mole fraction of ethanol.[18]

The single-ion values of $\Delta G_t°$ which they obtain, though quantitatively different from those of Part II, show the same general semi-quantitative features. Other points made by these authors will be discussed later in this Series.

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* The signs of the $\Delta G_t°$ values in Table 5 of Part II [1] should be negative, not positive.

[16] D. Feakins and R. P. T. Tomkins, unpublished results.

[17] C. L. de Ligny and M. Alfenaar, *Rec. Trav. chim.*, 1965, **84**, 81.

[18] A. Ben-Naim and S. Baer, *Trans. Faraday Soc.*, 1964, **60**, 1736.