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Entropies of Solution of Ions in Water

B. G. Cox*¹ and A. J. Parker

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Abstract: The entropies of solution of ions in water and the entropies of transfer from an ideal solution to aqueous solution have been obtained by assuming that the entropy of an ion in a crystal lattice is constant and independent of the lattice containing the ion and that the entropies of solution (*i.e.*, solid to liquid) of Ph_4As^+ and Ph_4B^- are equal. The values are internally consistent and agree favorably with entropies of solution and entropies of transfer calculated from the entropies of hydration (gas to liquid) reported by Frank and Evans. Our two assumptions lead to a value of $-3.9 \text{ cal deg}^{-1} \text{ mol}^{-1}$ for the absolute standard partial molal entropy of the proton in water. This is in excellent agreement with currently accepted values.

Since the papers of Frank and Evans² and Frank and Wen³ on the effect of ions on the structure of water, there have been many publications relating the changes in thermodynamic properties of water,⁴⁻⁹ containing various electrolytes, to the structure-making or structure-breaking effects of the ions concerned. Apart from the original paper by Frank and Evans,² in which the "structure-breaking entropy" of a number of monovalent ions was determined from entropies of solution, and a paper by Noyes,⁹ such discussions have tended to be qualitative rather than quantitative. In view of the current interest in the solvation of ions in nonaqueous solvents and in the free energies, enthalpies, and entropies of transfer of single ions from water to nonaqueous solvents,¹⁰ a simple and acceptable method of estimating the entropy changes which occur, when single ions are dissolved in water, would be of great value in aiding the interpretation of such changes.

Relative Entropies of Solution. If the solubility of an electrolyte, MX, and its heat of solution in water are known, then the entropy of solution of the electrolyte in water from the crystal state follows simply from the familiar relationships 1 and 2, where K_{sp} ,

$$\Delta G_s(\text{MX}) = -RT \ln K_{sp} \quad (1)$$

$$-T\Delta S_s(\text{MX}) = \Delta G_s(\text{MX}) - \Delta H_s(\text{MX}) \quad (2)$$

ΔG_s , ΔH_s , and ΔS_s are the solubility product, the standard free energy, enthalpy, and entropy, respectively, of a solution of MX referred to infinite dilution on the molal scale in water.

Latimer¹¹ has proposed a rule that there is little change in the entropy of a particular ion in different crystal lattices; *i.e.*, the entropy is independent of the lattices containing the ion to within about $\pm 3 \text{ cal deg}(\text{K})^{-1} \text{ g-ion}^{-1}$. Thus, it is possible to obtain a consistent and reasonable set of values of the entropy of solution of many cations relative to selected reference cations and anions, because a corollary of Latimer's rule is that $\Delta S_s(\text{ion})$ is independent of the lattice containing the ion. This requires that the difference between the entropies of solution of a pair of cations, as calculated from data for those cations with a series of counteranions (and *vice versa*), should be independent of the counterion, if the rule is valid. Values of $-298\Delta S_s$ at 25° on the molal scale can be calculated from ΔG_s and ΔH_s mainly in standard compilations.¹¹⁻¹³ Some additional data are in Table I.

Table II contains the entropies of solution of various

(1) Author to whom enquiries should be addressed at the Department of Chemistry, University of Stirling, Stirling, Scotland.

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(11) W. M. Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solution," 2nd ed, Prentice-Hall, Englewood Cliffs, N. J., 1952.

(12) V. B. Parker, "Thermal Properties of Aqueous Uni-Univalent Electrolytes," U. S. National Bureau of Standards, NSRDS-NBS2, Washington D. C., 1965.

(13) D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffe, "Selected Values of Chemical Thermodynamic Properties," U. S. National Bureau of Standards Circular 500, and supplementary notes 270-1 to 270-3.

Table I. Standard Entropies of Solution of Electrolytes in Water at 25° (Molal Scale in kcal mol⁻¹)^a

Salt	-298ΔS _s ^a	Salt	-298ΔS _s
NBu ₄ I	-0.6 ^b	AgBPh ₄	+3.4 ^e
KBPh ₄	+0.6 ^c	Ph ₄ AsI	-1.4 ^f
RbBPh ₄	-0.1 ^d	Ph ₄ AsClO ₄	-1.5 ^g
CsBPh ₄	-0.4 ^d	Ph ₄ AsBr	2.1 ^g

^a Calculated from ΔG_s - ΔH_s at 25°. ^b ΔG_s is 3.2 kcal mol⁻¹, this work; ΔH_s from R. Fuchs, J. L. Bear, and R. F. Rodewald, *J. Amer. Chem. Soc.*, **91**, 5797 (1969). ^c Solubility from R. Alexander, A. J. Parker, J. H. Sharp, and W. E. Waghorne, *ibid.*, **94**, 1148 (1972); ΔH_s from Y. C. Wu and H. L. Friedman, *J. Phys. Chem.*, **70**, 501 (1966). ^d Solubility from D. H. Berne and O. Popovych, *Anal. Chem.*, **44**, 817 (1972); ΔH_s as in *c*. ^e Solubility from I. M. Kolthoff and M. K. Chantooni, *Anal. Chem.*, **44**, 194 (1972); ΔH_s from ref 10. ^f Solubility as in *c*; ΔH_s from E. M. Arnett and D. R. McKelvey, *J. Amer. Chem. Soc.*, **88**, 2598 (1966). ^g Solubility from I. M. Kolthoff and M. K. Chantooni, *J. Phys. Chem.*, **76**, 2024 (1972); ΔH_s from C. V. Krishnan and H. L. Friedman, *J. Phys. Chem.*, **73**, 3934 (1969).

solution of both monatomic and complex ions are more or less independent of their lattice or origin. In Table IV we show that our mean entropies of solution of solid ions, relative to values for appropriate reference ions, compare very well with most of the entropies of solvation of gaseous ions relative to the same reference ions, as reported by Noyes,⁹ by Breck and Lin,¹⁴ and by Frank and Evans.² We note the discrepancies for manganese, iron, copper, and especially cobalt and nickel between our estimates and those of Noyes⁹ but cannot offer an explanation.

To a good approximation, the contribution of each atom to the molal entropy of a solid at 25° is given by eq 3,¹⁵ so that this also gives the molal entropy of a

$$S^{\circ}_{298} = \frac{3}{2}R \ln M_i - 0.94 \text{ cal deg(K)}^{-1} \text{ mol}^{-1} \quad (3)$$

solid monatomic ion of atomic weight M_i . The entropy of a gaseous monatomic ion is given by the Sackur-

Table II. Entropies of Solution (-298ΔS_s kcal mol⁻¹) at 25° of Cations in Water

Cation M ⁺	Anion X ⁻											Mean ^b	
	OH ⁻	F ⁻	Cl ⁻	Br ⁻	I ⁻	NO ₃ ⁻	SO ₄ ²⁻	ClO ₄ ⁻	HCO ₃ ⁻	BPh ₄ ⁻	S ²⁻		
(i) Monovalent Cations, M ⁺ , Relative to Rb ⁺ , <i>i.e.</i> , -298ΔS _s (MX) + 298ΔS _s (RbX) ^a													
Li ⁺	+6.5	+5.2	+5.1	+5.0	+4.5	+6.3	+5.6					+5.5	
Na ⁺	+3.3	+3.4	+3.1	+2.8	(-4.4) ^b	+2.8	+3.1	+3.3	+3.5		+2.9	+3.1	
K ⁺	+1.1		+0.8	+0.2	+0.3	+1.0	+1.0	+1.0	+1.8	+0.7	+0.7	+0.9	
Rb ⁺	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
Cs ⁺	+0.1	(-2.0) ^b	-0.4	+0.2	-0.2	-0.2	-0.1	+0.4	(-5.1) ^b	-0.3	-0.1	-0.2	
Ag ⁺		+4.4	+3.7	+3.4	+2.9	+3.5	+3.9	+3.6		+3.5		+3.6	
NH ₄ ⁺		1.0	0.8	0.9	0.4	1.3	1.7					+1.0	
Tl ⁺	-0.3		+0.7	+0.4	-0.9		+0.8					+0.1	
Ph ₄ As ⁺				+8.9	+6.6			+8.9				+8.1	
(ii) Divalent Cations, M ²⁺ , Relative to Sr ²⁺ , <i>i.e.</i> , -298ΔS _s (MX ₂) + 298ΔS _s (SrX ₂) ^a													
Be ²⁺			+11.2	+11.3	+11.1		+11.2					+11.2	
Mg ²⁺			+3.6	+4.4	+4.4	+3.4	+5.6					+4.3	
Ca ²⁺		+0.3	+0.8	+0.5	(-0.7) ^b	+1.1	0.0					+0.5	
Sr ²⁺	0.0	0.0	0.0	0.0	0.0	0.0	0.0					0.0	
Pb ²⁺	-2.8	-1.3	-3.3	-2.9	-3.7		-2.6					-2.8	
Ba ²⁺	-2.1	-2.5	-3.2	-3.9	-3.3	-2.4	-3.9					-3.0	
MN ²⁺			+2.9	+2.9	+2.4		+2.4					+2.7	
Fe ²⁺	+5.3	+5.2	+4.8	+4.5			+6.1					+5.2	
Co ²⁺	+5.9	+5.2	+4.9	+5.2	+5.4							+5.3	
Ni ²⁺		+5.6	+7.2	+7.7	+7.5		(+4.9) ^b					+7.0	
Cu ²⁺	+3.1	+4.5	+3.6	+3.9	+3.6		+3.5					+3.7	
Zn ²⁺	+5.1		3.9	4.4	+4.1		+4.8					+4.5	
Cd ²⁺	+2.7	(+3.9) ^b	+1.5	+1.1	+1.6		+2.5					+1.9	
Sn ²⁺	+0.2		-1.5	-0.7	-1.0							-0.8	

^a All values in this table calculated from ΔG_s and ΔH_s in ref 11-13 or Table I. Standard entropies of solution of rubidium salts in water at 25°, -298ΔS_s molal scale in kcal mol⁻¹, are: RbF, -3.0; RbCl, -6.1; RbBr, -6.8; RbI, -8.0; RbClO₄, -10.2; RbOH, -3.1; RbNO₃, -9.2; RbBPh₄, -0.1; RbHCO₃, -7.8; Rb₂S, -6.3; Rb₂SO₄, -5.2. Standard entropies of solution of strontium salts in water at 25°, as -298ΔS_s, kcal mol⁻¹, molal scale are: Sr(OH)₂, +10.0; SrF₂, +9.9; SrCl₂, +3.4; SrBr₂, +1.3; SrI₂, -0.9; Sr(NO₃)₂, -4.1; SrSO₄, +10.4; from ΔG_s - ΔH_s in ref 11-13. ^b Values in parentheses have been ignored in calculating the mean value.

monovalent and divalent cations (M) relative to Rb⁺ and Sr²⁺, respectively, for a number of counteranions X⁻ (*e.g.*, -298ΔS_s(MX) + 298ΔS_s(RbX)) at 25°. Table III contains entropies of solution of various monovalent anions (X) relative to Cl⁻ for a variety of counteranions M⁺ (*i.e.*, -298ΔS_s(MX) + 298ΔS_s(MCl)) at 25°. The entropies of solution of various rubidium, strontium, and chloride salts are shown in footnotes to Tables II and III. From these values, together with the relative values in Tables II and III, the entropies of solution of electrolytes containing all of the various ions listed in the standard compilations¹¹⁻¹³ can be obtained.

Although there is some scatter, the observed differences in Tables II and III confirm that the entropies of

Tetrode equation (eq 4), so that for formation of the same

$$S^{\circ}_{298} = \frac{3}{2}R \ln M_i + 25.9 \quad (4)$$

standard state in solution, entropies of *solution* of solid monatomic ions are more positive by 26.8 cal deg⁻¹ mol⁻¹ (the entropy of sublimation) than are the entropies of *solvation* of gaseous monatomic ions. However, entropies of solution and entropies of solvation of a series of monatomic ions relative to a reference ion should be the same, as is roughly established in Table IV. Some of the discrepancies noted there are undoubtedly due to differences of source material.

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(15) G. N. Lewis and M. Randall, "Thermodynamics," revised ed., K. S. Pitzer and L. Brewer, Ed., McGraw-Hill, New York, N. Y., 1961, p 518.

Table III. Entropies of Solution ($-T\Delta S$ kcal mol $^{-1}$ at 25°) of Anions in Water, All Relative to Chloride Ion, *i.e.*, $-298\Delta S_s(\text{MX}) + 298\Delta S_s(\text{MCl})^a$

Anions X ⁻	Cations M ⁺													Mean ^b			
	Li ⁺	Na ⁺	K ⁺	Rb ⁺	Cs ⁺	Ag ⁺	Mg ²⁺	Ca ²⁺	Sr ²⁺	Ba ²⁺	Fe ²⁺	Cu ²⁺	Pb ²⁺		Co ²⁺	Al ³⁺	NEt ₄ ⁺
OH ⁻	+4.4	+3.2	+3.1	+3.0	+3.5	+3.8	0.0	+3.0	+3.3	+3.9	+3.4	+3.1	+3.6	+3.8			+3.5
F ⁻	+3.2	+3.4	0.0	+3.1	(+1.5) ^b	0.0	0.0	0.0	+3.3	+3.6	0.0	+3.7	+4.3	+3.4	+4.4		+3.5
Cl ⁻	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Br ⁻	-0.8	-1.0	-1.3	-0.7	-0.1	-1.0	-0.7	-1.2	-1.1	-1.4	-1.3	-0.9	-0.9	-0.9	-1.4	(-5.3) ^b	-1.0
I ⁻	-2.5	-2.4	-2.4	-1.9	-1.7	-2.7	-1.8	-2.9	-2.2	-2.2	-2.5	-2.2	-2.4	-1.9	-3.0	(-8.5) ^b	-2.3
NO ₃ ⁻	(1.9) ^b	-3.4	-3.0	-3.1	-2.9	-3.3	-4.8	-3.7	-3.7	-3.8							-3.3
ClO ₄ ⁻		-4.1	-4.1	-4.3	-3.5	-4.4				(-6.3) ^b							-4.2
HCO ₃ ⁻		-1.3	-0.9	-1.7	(-6.5) ^b												-1.3
BPh ₄ ⁻			+5.9	+6.0	+6.1	+5.8											+6.0

^a All values in this table calculated from ΔG_s and ΔH_s in ref 11-13 or Table I. Standard entropies of solution of chlorides in water at 25°, as $-298\Delta S_s$ kcal mol $^{-1}$, are: LiCl, -1.0; NaCl, -3.0; KCl, -5.3; RbCl, -6.1; CsCl, -6.5; AgCl, -6.5; MgCl₂, -2.4; MgCl₂, +7.0; CaCl₂, +4.2; SrCl₂, +3.4; BaCl₂, 0.2; FeCl₂, 8.6; CuCl₂, 7.0; PbCl₂, 0.1; CoCl₂, 8.3; AlCl₃, 22.3. ^b Values in parentheses have been ignored in estimating the mean value.

Table IV. Entropies of Solution of Single Ions ($-298\Delta S_s$ kcal mol $^{-1}$) at 25° vs. a Reference Ion

Ion	Mean (Table II)	Frank and Evans ^a	Noyes ^b	Breck and Lin ^c
(a) Monovalent Cations Relative to Rb ⁺				
H ⁺			4.9	
Li ⁺	5.5	4.9	5.6	5.3
Na ⁺	3.1	3.2	3.3	2.9
K ⁺	0.9	0.6	0.8	0.6
Rb ⁺	0.0	0.0	0.0	0.0
Cs ⁺	-0.2	-0.5	-0.2	-0.5
Ag ⁺	3.6		3.8	3.5
NH ₄ ⁺	1.0	2.2		
Tl ⁺	0.1		0.5	0.3
Ph ₄ As ⁺	8.1			
(b) Monovalent Anions Relative to Cl ⁻ (Table III)				
OH ⁻	3.5			
F ⁻	3.5	4.3	4.1	4.1
Cl ⁻	0.0	0.0	0.0	0.0
Br ⁻	-1.0	-1.2	-1.2	-1.1
I ⁻	-2.3	-2.4	-2.7	-2.7
NO ₃ ⁻	-3.3	-3.0		
ClO ₄ ⁻	-4.2			
HCO ₃ ⁻	-1.3			
BPh ₄ ⁻	+6.0			
(c) Divalent Cations Relative to Ca ²⁺ (Table II)				
Be ²⁺	10.7		10.8	
Mg ²⁺	3.8	5.6	4.0	4.0
Ca ²⁺	0.0	0.0	0.0	0.0
Sr ²⁺	-0.5	-0.5	-0.5	-0.5
Pb ²⁺	-3.3		-4.0	
Ba ²⁺	-3.5	-2.9	-3.6	-3.7
Mn ²⁺	2.2		3.5	
Fe ²⁺	4.7		6.0	
Co ²⁺	4.8		9.2	
Ni ²⁺	6.5		9.4	
Cu ²⁺	3.2	5.0	4.6	
Zn ²⁺	4.0	4.8	4.1	4.1
Cd ²⁺	1.4		1.4	1.3
Sn ²⁺	-1.3		-1.6	

^a Reference 2. ^b Reference 9. ^c Reference 14.

We have used a very simple method for determining the entropies of solution of anions and cations, relative to a reference anion or cation. This does not demand any knowledge of gas phase entropies or of absolute entropies of ions in aqueous solution; one only needs to know ΔG_s and ΔH_s for the solution of electrolytes.

Single Ion Entropies of Solution. In order to place the values in Table IV, for various cations and anions which are relative to reference ions, on the one absolute scale, it is necessary to make use of an extrathermodynamic assumption. If one accepts our recommendation, which is justified elsewhere,¹⁰ that the entropies of solution of the tetraphenylarsonium and tetraphenylboride ions are equal, $\Delta S_s(\text{Ph}_4\text{As}^+) = \Delta S_s(\text{Ph}_4\text{B}^-)$, then single ion entropies of solution can be readily obtained by application of eq 5 and 6 to the data in Tables I-III.

$$\Delta S_s(\text{M}^+) - \Delta S_s(\text{X}^-) = \Delta S_s(\text{MBPh}_4) - \Delta S_s(\text{Ph}_4\text{As X}) \quad (5)$$

$$\Delta S_s(\text{M}^+) + \Delta S_s(\text{X}^-) = \Delta S_s(\text{MX}) \quad (6)$$

lent cations and anions. Application of this assumption to the results in Tables I-III leads to values of $-T\Delta S_s(\text{Ph}_4\text{As}^+) = -T\Delta S_s(\text{BPh}_4^-) = 4.0$ kcal g-ion $^{-1}$ ($T = 298^\circ\text{K}$) and thus $-T\Delta S_s(\text{Ph}_4\text{AsBPh}_4) = 8.0$ kcal

Table V. Standard Entropies of Solution^c and Entropies of Transfer^d of Ions to Water at 25°, Molal Scale, Assumptions $\Delta S_s(\text{Ph}_4\text{As}^+) = \Delta S_s(\text{Ph}_4\text{B}^-)$

Ion	$-298\Delta S_s^a$ kcal mol ⁻¹	ΔS_{tr}^d cal deg ⁻¹ mol ⁻¹
H ⁺	(0.8) ^b	(-13.7) ^b (-14.8) ^f
Li ⁺	1.4	-15.7 (-15.8) ^f
Na ⁺	-1.0	-7.6 (-10.1) ^f
K ⁺	-3.2	-0.3 (-1.5) ^f
Rb ⁺	-4.1	2.7 (0.7) ^f
Cs ⁺	-4.3	3.4 (2.5) ^f
Ag ⁺	-0.5	-9.3
Tl ⁺	-4.0	2.4
NH ₄ ⁺	-3.1	-0.6
NBu ₄ ⁺	4.3 ^e	-25.3
Ph ₄ As ⁺	4.0	-24.4
Be ²⁺	18.4	-72.7
Mg ²⁺	11.5	-49.6 (-60.4) ^f
Ca ²⁺	7.6	-36.5 (-41.7) ^f
Sr ²⁺	7.2	-35.2 (-39.9) ^f
Ba ²⁺	4.2	-25.1 (-31.8) ^f
Mn ²⁺	9.9	-40.9
Fe ²⁺	12.4	-52.6
Co ²⁺	12.5	-52.9
Ni ²⁺	13.8	-57.3
Cu ²⁺	10.9	-47.6 (-58.2) ^f
Zn ²⁺	11.7	-50.3 (-57.5) ^f
Cd ²⁺	9.4	-42.5
Sn ²⁺	6.4	-32.5
Pb ²⁺	4.4	-25.8
Al ³⁺	27.1	-101.9 (-109.7) ^f
Sc ³⁺	20.7	-80.5
Y ³⁺	23.2	-88.8
Cr ³⁺	25.6	-96.9
Fe ³⁺	25.0	-94.8 (-96.7) ^f
OH ⁻	1.5	-16.0
F ⁻	1.4	-15.7 (-17.1) ^f
Cl ⁻	-2.0	-4.3 (-2.8) ^f
Br ⁻	-3.0	-0.9 (+1.1) ^f
I ⁻	-4.3	3.4 (5.3) ^f
N ₃ ⁻	-4.5	4.1
HCO ₃ ⁻	-3.3	0.1
NO ₃ ⁻	-5.3	6.8 (7.0) ^f
ClO ₃ ⁻	-5.8	8.5
ClO ₄ ⁻	-6.2	9.8
BPh ₄ ⁻	4.0	-24.4
S ²⁻	2.3	-18.7
SO ₄ ²⁻	3.1	-21.4 (-26.2) ^f
SO ₃ ²⁻	5.6	-29.8
CO ₃ ²⁻	6.1	-31.5
PO ₄ ³⁻	19.2	-75.4

^a Calculated from mean values in Tables II-IV as described in the text. ^b Estimated from $-298\Delta S_s = 4.9$ kcal mol⁻¹ relative to rubidium as quoted by Noyes (ref 9); cf. Table IV. ^c The entropy of solution, ΔS_s , is the entropy of transfer of an ion from solid to a solution of unit molality in water. ^d The entropy of transfer is for transfer of an ion to water from a hypothetical ideal liquid state of unit molality, that is, of mole fraction 1/56.5, so that $\Delta S_{tr} = \Delta S_s - 11$ (see text). ^e Quoted value is from NBu₄I only. ^f Values in parentheses are $\Delta S_{tr} = -\Delta S_v + 23.8$ where ΔS_v are values given by Frank and Evans, ref 2, and the 23.8 cal deg⁻¹ g-ion⁻¹ allows for the reduction in free volume on transfer from the gas to the liquid phase (see text).

mol⁻¹, when values for various Ph₄As⁺ and BPh₄⁻ salts are averaged. This may be compared with a value of $-T\Delta S_s(\text{Ph}_4\text{AsBPh}_4) = 7.8$ kcal mol⁻¹ that may be obtained from the ΔH_s values of Choux and Benoit,¹⁶ which indicate 15.8 kcal mol⁻¹ for the enthalpy of solution of Ph₄AsBPh₄ in water, together with our value of¹⁷

(16) G. Choux and R. L. Benoit, *J. Amer. Chem. Soc.*, **91**, 6221 (1969).

(17) B. G. Cox and A. J. Parker, *J. Amer. Chem. Soc.*, **94**, 3674 (1972).

$\Delta G_s(\text{Ph}_4\text{AsBPh}_4) = 23.6$ kcal mol⁻¹ in water. Table V lists the values of the single ion entropies of solution, according to the above assumption.

Entropies of Transfer from an Ideal Solvent to Water.

In order to isolate entropy values specifically associated with the effect of ions interacting with water, as distinct from the effect of change of state, it is necessary to allow for the fact that when an ion is transferred from the solid to a liquid state there will always be an increase in entropy due to the increased mobility (translational entropy) in the liquid state and the increased volume. This is independent of any entropy effects due to ion-solvent and solvent-solvent interactions. To allow for this it is necessary to subtract from the values of ΔS_s in Table V the entropy of transfer of an ion from a solid to an ideal (as defined by Raoult's law) liquid state of unit molality. We estimate this as 11 cal deg⁻¹ mol⁻¹ made up of 3 cal deg⁻¹ mol⁻¹ for the entropy of melting to form an ideal "solution" of unit mole fraction and 8 cal deg⁻¹ mol⁻¹ ($2.3R \log 55.5$) for dilution to a standard state of unit molality. The value of 3 cal deg⁻¹ mol⁻¹ for the entropy of melting corresponds to that observed for inert gases and is in the range of 2.0 to 3.5 cal deg⁻¹ mol⁻¹ observed for both monatomic solids and infinite lattices of single ions.¹⁵ The entropies of transfer ($\Delta S_{tr,ion}$) of the various ions, from an ideal structureless solution (as defined by Raoult's law) of unit molality to a solution of unit molality in water, are thus $\Delta S_{s,ion} - 11$ cal deg⁻¹ mol⁻¹. They are also listed in Table V as $\Delta S_{tr,ion}$.

Frank and Evans² split up the entropy values for electrolytes into those for individual ions in aqueous solution by the Eastman-Latimer assumption,¹¹ which gives the generally accepted^{9,18-21} standard partial molal entropies for aqueous chloride and hydrogen ions, of $S^\circ(\text{Cl}^-) = 18.1$ cal deg⁻¹ g-ion⁻¹ and $S^\circ(\text{H}^+) = -4.6 \pm 1$ cal deg⁻¹ g-ion⁻¹. It is interesting to note that our quite different procedure, involving entropies of solution and the assumption that $\Delta S_s(\text{Ph}_4\text{As}^+) = \Delta S_s(\text{Ph}_4\text{B}^-)$, leads to $S^\circ(\text{H}^+) = -3.9$ cal deg⁻¹ g-ion (vide infra) and thus gives almost the same values for $\Delta S_{tr,ion}$ as do those based on a value of 18.1 cal deg⁻¹ g-ion⁻¹ for the standard partial molal entropy of hydrated chloride ion.² Frank and Evans² recorded as ΔS_v a limited number of molal entropies of vaporization of ions at 25° from a hypothetical mole fraction of unity in aqueous solution to a hypothetical gas state at 1 atm of pressure. They allowed for restrictions to vibration and rotation in the liquid state for complex ions like NO₃⁻ and SO₄²⁻. They suggested that the loss of entropy when a gas dissolves, caused by the reduction in free volume, is about 20-25 cal deg⁻¹ mol⁻¹ based on their standard states. Using a molal entropy of sublimation of a monatomic ion of 26.8 cal deg⁻¹ g-ion⁻¹ (eq 3 and 4) and converting the Frank and Evans² standard state to a unimolal solution ($\Delta S_v - 8.0$ cal deg⁻¹ mol⁻¹), allowing for the entropy change from solid to our ideal solution (11 cal deg⁻¹ mol⁻¹), gives the rela-

(18) D. D. Eley and M. G. Evans, *Trans. Faraday Soc.*, **34**, 1093 (1938).

(19) R. W. Gurney, "Ionic Processes in Solution," McGraw-Hill, New York, N. Y., 1953, p 257; W. M. Latimer, *Chem. Rev.*, **18**, 349 (1936).

(20) H. D. Crockford and J. L. Hall, *J. Phys. Colloid Chem.*, **54**, 731 (1950).

(21) F. M. Goyan, E. E. Morse, R. G. Preston, and M. B. Young, *J. Amer. Chem. Soc.*, **72**, 4411 (1950).

tionship $\Delta S_{tr}(\text{ion}) = -\Delta S_v + 23.8 \text{ cal deg}^{-1} \text{ g-ion}^{-1}$. Values of $-\Delta S_v + 23.8$ (in parentheses) from Frank and Evans² are compared with our $\Delta S_{tr}(\text{ion})$ in Table V. The agreement between our assumption that $\Delta S_s(\text{Ph}_4\text{As}^+) = \Delta S_s(\text{Ph}_4\text{B}^-)$ and the Eastman-Latimer assumption¹¹ that $S^\circ(\text{Cl}^-) = 18.1 \text{ cal deg}^{-1} \text{ g-ion}^{-1}$ is remarkably good in most cases and is within $2 \text{ cal deg}^{-1} \text{ g-ion}^{-1}$ for monovalent ions.

An advantage of our method over that of Frank and Evans for estimating free energies of transfer of single ions from an ideal liquid to water is that it only requires data for changes in entropy on going from solid to aqueous solution (ΔG_s and ΔH_s) and a value of $3 \text{ cal deg}^{-1} \text{ mol}^{-1}$ for the entropy of ideal melting. It can be applied to many more types of ion than the simple monatomics. There is no need for absolute partial molal entropies, entropies of crystals, or gas phase entropies, and we come to much the same conclusions as to values of ΔS_{tr} .

Standard Partial Molal Entropy of H^+ in Aqueous Solution, $S^\circ(\text{H}_{aq}^+)$. It is of interest to apply our assumption concerning the equality of entropies of solution of Ph_4As^+ to BPh_4^- to the determination of the standard partial molal entropy of H^+ in aqueous solution $S^\circ(\text{H}_{aq}^+)$. From the work of Latimer¹¹ we may say that to a good approximation, in the crystal KCl , $S^\circ(\text{K}_{(c)}^+) = S^\circ(\text{Cl}_{(c)}^-) = \frac{1}{2}S^\circ(\text{KCl}_{(c)})$ as the atomic weights of K^+ and Cl^- are very similar (eq 3). From the measured value^{12,13} of $S^\circ(\text{KCl}_{(c)}) = 19.7 \text{ cal deg}^{-1} \text{ mol}^{-1}$ we then have $S^\circ(\text{K}_{(c)}^+) = 9.9 \text{ cal deg}^{-1} \text{ mol}^{-1}$. From Table V it can be seen that, according to the assumption that $\Delta S_s(\text{Ph}_4\text{As}^+) = \Delta S_s(\text{BPh}_4^-)$, $\Delta S_s(\text{K}^+)$ is $+10.7 \text{ cal deg}^{-1} \text{ mol}^{-1}$ where $\Delta S_s(\text{K}^+)$ is the entropy of solution of K^+ from the crystal to aqueous solution. These figures give $S^\circ(\text{K}_{aq}^+) = 20.6 \text{ cal deg}^{-1} \text{ mol}^{-1}$. This value corresponds to a value of $S^\circ(\text{H}_{aq}^+) = -3.9 \text{ cal deg}^{-1} \text{ mol}^{-1}$ as Breck and Lin¹⁴ show that $S^\circ(\text{K}_{aq}^+) - S^\circ(\text{H}_{aq}^+) = 24.5 \text{ cal deg}^{-1} \text{ mol}^{-1}$. This value of $S^\circ(\text{H}_{aq}^+) = -3.9 \text{ cal deg}^{-1} \text{ mol}^{-1}$ may be compared with previously reported values of $S^\circ(\text{H}_{aq}^+)$ of -4.6 ,¹⁵ -2.1 to -3.4 ,²⁰ -3.3 ,⁹ and -5.5 .^{14,19}

Discussion

Our values of $\Delta S_{tr}(\text{ion})$ in Table V show the entropy changes associated with changes in water-water interactions and the introduction of ion-water interactions, when an ion is dissolved in water. Since our values are comparable to those of Frank and Evans,² once adjustments have been made, our discussion is not in conflict with their ideas.

Two features of the results in Table V stand out.

(i) The entropies of transfer of monovalent ions from our ideal solvent to water range from $+10$ to $-15 \text{ cal deg}^{-1} \text{ mol}^{-1}$. This is consistent with the generally accepted model² for solvation of the first kind,⁸ that solution of ions in water produces a decrease in entropy in a region in the immediate vicinity of the ion but an increase in entropy in a region further from the ion. The latter is due to disruption of the water structure by the solvated ions, whose bound water molecules are incorrectly oriented to fit into the H-bonded structure of water. The increase in entropy predominates for large ions of low charge density, like cesium and perchlorate. Since it is an increase in entropy relative to a situation in which the solvent has no order and

the ion induces no order, the positive values of $\Delta S_{tr}(\text{ion})$ demand that there be a net disordering of water in solutions of these ions. A disordered region between the ion centered order and the bulk water structure must be present if the assumptions are valid. For ions with higher charge density, including the divalent ions, the very negative values of ΔS_{tr} suggest that the effect of the region, in which there is orientation of water molecules in the immediate vicinity of the ion, predominates over the effect of the disordered region.

(ii) The ΔS_{tr} values for transfer of Ph_4As^+ , BPh_4^- , and NBu_4^+ to water are opposite to those predicted from the behavior of large ions of low charge density, like cesium or iodide. The greatly decreased entropy closely resembles that when typical nonelectrolytes such as benzene¹⁷ ($\Delta S_{tr} = -23 \text{ cal deg}^{-1} \text{ mol}^{-1}$) are transferred to water from an ideal solution. The effect is due to solvation of "the second kind"¹⁸ for these large hydrophobic ions. The solvent makes its own structure, which is a concave water surface, about the hydrophobic ligands. We believe that the structure of this surface is much the same, whether it be formed about Ph_4As^+ , Ph_4B^- , or indeed the unchanged species Ph_4C . Thus, although water is orientated differently about smaller anions like F^- and smaller hydrophilic cations like K^+ , the orientation is much the same about large insulated ions like Ph_4As^+ and Ph_4B^- . Thus, the assumption, $\Delta S_{tr}(\text{Ph}_4\text{As}^+) = \Delta S_{tr}(\text{Ph}_4\text{B}^-)$, is much more reasonable than assumptions of the type used by Kortum and Bockris,²² which equate entropies of hydration of K^+ and F^- . The entropies of hydration of Ph_4As^+ and Ph_4B^- are effectively the entropies of hydration of four tetrahedrally grouped phenyl groups. An important point in favor of our assumption as noted is that it leads to values of $S^\circ(\text{Cl}^-) = 18 \pm 1 \text{ cal deg}^{-1} \text{ g-ion}^{-1}$ and $S^\circ(\text{H}^+) = 4 \pm 1 \text{ cal deg}^{-1} \text{ g-ion}^{-1}$, in agreement with those which have been accepted by many chemists^{9,14,18-20} for the past half-century.

In discussing the behavior of simple monovalent cations and anions, Frank and Evans² used a model in which it was assumed that the loss of entropy resulting from the orientation of four water molecules in the immediate neighborhood of such ions (*i.e.*, in the first solvent shell) was constant ($12 \text{ cal deg}^{-1} \text{ g-ion}^{-1}$). The variation in the overall entropy of solution with different ions, once their free volume correction of $20 \text{ cal deg}^{-1} \text{ g-ion}^{-1}$ for gas to liquid was made, was caused by different effects of the solvated ions on the structure of water. Thus, Li^+ and F^- , plus their first solvent shell, were said to be structure makers (addition of the solvated ion results in loss of entropy) whereas the other ions, plus their first solvent shell, were structure breakers, the structure-breaking effect increasing with increasing size of the ion. Our values of $\Delta S_{tr}(\text{ion})$ would lead to much the same conclusion if we accept the value of $12 \text{ cal deg}^{-1} \text{ g-ion}^{-1}$ entropy loss for formation of the solvated ion.

Assuming that it is reasonable to attempt to divide up the observed entropy effects into effects in the immediate neighborhood of the ion and effects of the "solvated" ion on the water structure, then further information on this problem may be obtained by considering entropies of transfer of ions from water to

(22) G. Kortum and J. O'M. Bockris, "Textbook of Electrochemistry," Elsevier, New York, N. Y., 1951, p 123.

selected nonaqueous solvents. Most such solvents, unlike water, show no anomalous entropy behavior when nonpolar solutes are dissolved in them, and when ions are dissolved in them, the main entropy effects are confined to "freezing" of solvent molecules in the vicinity of the ion. These effects are indicated by the entropies of fusion of the nonaqueous solvents, which are greater than that for water.²³

The entropies of transfer of simple monovalent cations, M^+ , and anions, X^- , except lithium, from water to a variety of nonaqueous solvents, including acetonitrile, dimethylformamide, dimethyl sulfoxide, sulfolane, and *N*-methylpyrrolidone, show an almost constant loss of entropy of 20 cal deg⁻¹ g-ion⁻¹ (*i.e.*, 40 cal deg⁻¹ mol⁻¹ for transfer of electrolyte MX from water).^{16,23} Lithium values are less certain but show a smaller loss of entropy of 10 cal deg⁻¹ g-ion⁻¹ on transfer from water. If we assume that much the same number of solvent molecules (eq 4) are frozen about the ion in water as in the nonaqueous solvents, then the entropy increase associated with breaking the hydrogen-bonded structure of bulk water is at least 20 cal deg⁻¹ g-ion⁻¹ greater than for the breaking up of structures of other solvents. The entropy increase associated with "breaking the water structure" is the combination of breaking water structure (a) by forming a new ion-centered structure in the first solvation shell and (b) by creating a destructured region between the ion-centered structure and the bulk water-centered structure.

The large structure-breaking entropy effect of simple monovalent ions in water is peculiar to that solvent and favors solvation of simple ions in water by about 6 kcal mol⁻¹ at 25°, relative to most other solvents. Data for multivalent ions are not yet available.

The value of 20 cal deg⁻¹ g-ion⁻¹ is probably a lower limit to the combined structure-breaking effects of monovalent ions on water. This is because the nonaqueous solvents themselves will have some structure and for many small ions of high ionic potential in their respective solutions, more water molecules, than other

solvent molecules, will be "frozen" about the ion. Water has the ability, which dipolar aprotic solvents lack, of transferring charge from the first solvation shell to a second or third shell *via* hydrogen bonds. Cations with their water ligands are very powerful hydrogen-bond donors. Hydrated lithium ion in particular would be a very powerful hydrogen-bond donor and a greater number of waters than nonaqueous solvent molecules in the respective solvated lithium ions may explain the smaller loss in entropy when Li⁺ is transferred from water to nonaqueous solvents.

As expected, entropies of transfer of "organic" ions such as Ph₄As⁺, BPh₄⁻, and R₄N⁺ show entirely opposite behavior (there is a large increase in entropy when these ions are transferred to nonaqueous solvents,^{16,23} a behavior typical of transfer of nonelectrolytes). Ph₄As⁺ and BPh₄⁻ show increases of about 17 cal deg⁻¹ g-ion⁻¹ when transferred from water, irrespective of the nonaqueous solvent to which they are transferred. This suggests that the loss of *ca.* 24 cal deg⁻¹ g-ion⁻¹ when such ions are transferred from our ideal solvent to water is mainly due to a structure-making effect as water forms a surface about these ions.

Our picture of the entropy changes associated with dissolving a simple monovalent ion in water is one in which there is a significant loss of entropy because of structuring various numbers of water molecules in the immediate vicinity of the ion. The loss will depend on the radius of the ion (*i.e.*, more than 35 cal deg⁻¹ g-ion⁻¹ for Li⁺ to about 16 cal deg⁻¹ g-ion⁻¹ for Cs⁺ and I⁻). This is opposed by an entropy increase of at least 20 cal deg⁻¹ g-ion⁻¹ resulting from two types of structure breaking of the bulk water by the ion, one due to formation of a new structure, the second due to formation of a region of disordered water. At the present time there are insufficient data on the transfer of multivalent ions to nonaqueous solvents for an analysis of the very large losses in entropy which are observed when they are dissolved in water. However, it is clear that there is more than one layer of "frozen" water about ions such as Be²⁺, Zn²⁺, and Fe³⁺ and the entropy component due to structuring water about these ions is much greater than 35 cal deg⁻¹ g-ion⁻¹.

(23) B. G. Cox, G. A. Hedwig, A. J. Parker, and D. W. Watts, *J. Amer. Chem. Soc.*, submitted for publication.