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

**PART 2: ENTHALPIES AND ENTROPIES OF  
TRANSFER TO NONAQUEOUS SOLVENTS**

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## Thermodynamic functions of transfer of single ions from water to nonaqueous and mixed solvents: Part 2—Enthalpies and entropies of transfer to nonaqueous solvents

Abstract - Literature data on the enthalpies and entropies of transfer of ions from water to non-aqueous solvents to the end of 1982 are compiled and evaluated according to stated criteria, including the extra-thermodynamic assumption. Data, for which the tetraphenylarsonium tetraphenylborate assumption was not used were assigned low weights in the evaluation. The entropy data were subjected to the additional criterion of yielding with the enthalpy data the previously established Gibbs free energy data. Selected values are suggested on the basis of a weighted averaging procedure.

### INTRODUCTION

The literature has been surveyed to the end of 1982, and a critical evaluation of the data has been made.

Similarly to the previous report (ref. 1), which has dealt with the Gibbs free energies of transfer of individual ions from water to non-aqueous solvents, this report too concerns the transfer of single ions. Extrathermodynamic assumptions are necessary for dividing the thermodynamic data for complete electrolytes into ionic contributions. Those cases, where the data have not been treated in this manner by the original authors, and where this division cannot either be carried out by the compiler, have been left out from this survey. Included therefore are only cases where this division has been or can be made. These are classified into the following categories:

- (i) The division into the ionic contributions has been or can be made according to a reliable extrathermodynamic assumption. These cases have been given full weight in the evaluation.
- (ii) The division has been made according to a not completely satisfactory extrathermodynamic assumption, but data have been provided for both cations and anions, and data are available for some of these ions, that belong to category (i). In such cases adjustments have been made, the criterion of additivity being adhered to. Such data have been given less than full weight in the evaluation.
- (iii) The division has been made according unsatisfactory extrathermodynamic assumptions. Such data have been recorded in the compilation but have been given zero weight in the evaluation.

Contrary to the case of the Gibbs free energies of transfer, only the "reference electrolyte" assumption has been used for the enthalpies of transfer, since nothing that corresponds to the "Fic/Foc" assumption is available for the enthalpies. Entropies of transfer of individual ions have been estimated by means of the "reference electrolyte" assumption too, but also by means of other ones. These include the use of electrostatic terms (the temperature derivative of the Born expression) and so-called neutral-solute terms in theoretical calculations, and the use of the correspondence principle.

The most widely used "reference electrolyte" assumption, the  $\text{Ph}_4\text{AsBPh}_4$  one, is that  $\Delta H_t^\circ(\text{Ph}_4\text{As}^+, \text{W} \rightarrow \text{S}) = \Delta H_t^\circ(\text{BPh}_4^-, \text{W} \rightarrow \text{S})$  and similarly  $\Delta S_t^\circ(\text{Ph}_4\text{As}^+, \text{W} \rightarrow \text{S}) = \Delta S_t^\circ(\text{BPh}_4^-, \text{W} \rightarrow \text{S})$ , for the transfer from water, W, to all solvents S, at any temperature. This is tantamount to assuming that the  $\text{Ph}_4\text{AsBPh}_4$  assumption that has been used for the Gibbs free energy of transfer at a given reference temperature (usually 298.15 K) (ref. 1) is valid for all temperatures. It is indeed difficult to see a reason why this assumption should not be valid at other temperatures, provided its validity at one is accepted, on the grounds of the largeness, low charge, and nearly same size of the constituent ions of this reference electrolyte.

Systems where the  $\text{Ph}_4\text{AsBPh}_4$  assumption has been used are assigned to category (i). The care with which the primary data have been collected and the adequacy of the adjustment of the data to the reference state of infinite dilution (by means of heats of dilution, in the case of enthalpies) have also been taken into account in the weight given to the data from a given source. Lower weights have been given to cases belonging to category (ii), and in cases where the criterion of additivity of cation and anion values to give agreement with reliable complete electrolyte data could not be applied.

In order to permit comparisons and evaluation, all the values have been selected for one temperature, 298.15 K, except for those solvents for which this temperature is outside the liquid range (e.g., tetramethylene sulfone or ammonia). The data for the entropies have been converted to the molar scale ( $\text{mol/dm}^3$ ) (ref. 2). The units  $\text{kJ/mol}$  have been used for the enthalpies of transfer and  $\text{J/K.mol}$  for the entropies.

The selected quantities have been obtained as the weighted means of the reported values for each ion and solvent. Each report of an author or group of authors has been treated separately, even if it just repeats the values given in a previous report, since it reaffirms in doing so the author's acceptance of their validity. In those cases where the enthalpy results from reliable independent sources agree within ca. 1 to 2  $\text{kJ/mol}$ , the selected value is presented to one place beyond the decimal point, and may be considered as recommended. For the entropies, a recommended value is based on values from reliable independent sources varying by not more than ca. 3 to 5  $\text{J/K.mol}$  from one another. These are given as integral values. In other cases no confirmation from independent sources has come forth, or the data from apparently reliable sources differ by more than the above-mentioned limits. The selected value is then given in parenthesis, and should be considered as tentative, subject to further study and confirmation. In many cases, however, no selection could be made at all, if the data all belong to categories (ii) or (iii).

Since  $\Delta S_{\text{t}}^{\circ}$  is generally obtained from experimental values of  $\Delta G_{\text{t}}^{\circ}$  and  $\Delta H_{\text{t}}^{\circ}$ , it is mandatory for the selected values of  $\Delta S_{\text{t}}^{\circ}$  to be consistent with the quantity  $[\Delta H_{\text{t}}^{\circ}(\text{selected}) - \Delta G_{\text{t}}^{\circ}(\text{selected})]/T$ . This is found to be generally the case within the expected error of  $\pm 6 \text{ J/K.mol}$ . In the few cases where this is not adhered to, the weighted mean  $\Delta S_{\text{t}}^{\circ}$  value is put in brackets []. For the solvent N,N-dimethylformamide (DMF) this seems to be systematically the case, and the values selected for tetraphenylborate (and/or tetraphenylarsonium) are thought to be at fault. An adjustment of +14  $\text{J/K.mol}$  to the cation values and -14  $\text{J/K.mol}$  to the anion values corrects this situation.

The selected values and the compilation of the data are presented in the corresponding sections below.

#### LIST OF SOLVENTS AND ABBREVIATIONS OF IONS

$\Delta H_{\text{t}}^{\circ}$  and  $\Delta S_{\text{t}}^{\circ}$  data are available for those solvents from this list marked with (H) and (S), respectively.

Deuterium oxide ( $\text{D}_2\text{O}$ )(H,S)	N-Ethylacetamide (H)
Methanol ( $\text{MeOH}$ )(H,S)	N,N'-Dimethylformamide (DMF)(H,S)
Ethanol ( $\text{EtOH}$ )(H,S)	N,N'-Dimethylacetamide (H)
1-Propanol ( $\text{PrOH}$ )(H,S)	N-Methylpyrrolidone (NMPy)(H,S)
1,2-Dimethoxyethane (S)	N,N,N',N'-Tetramethylurea (H)
Tetrahydrofuran (S)	Acetonitrile ( $\text{MeCN}$ )(H,S)
Acetone (S)	Nitromethane (H,S)
Propylene carbonate (PC)(H,S)	Pyridine (H)
Ammonia (H,S)	Dimethylsulfoxide (DMSO)(H,S)
Formamide (FA)(H,S)	Tetramethylene sulfone (TMS)(H,S)
N-Methylformamide (H,S)	Hexamethyl phosphoric triamide (H,S)
N-Methylacetamide (H)	1,1-Dichloroethane (S)
	1,2-Dichloroethane (H,S)

$\text{Me}_4\text{N}^+ = (\text{CH}_3)_4\text{N}^+$ ;  $\text{Et}_4\text{N}^+ = (\text{C}_2\text{H}_5)_4\text{N}^+$ ;  $\text{Pr}_4\text{N}^+ = (\text{C}_3\text{H}_7)_4\text{N}^+$ ;  $\text{Bu}_4\text{N}^+ = (\text{C}_4\text{H}_9)_4\text{N}^+$ ;  
 $\text{Pn}_4\text{N}^+ = (\text{C}_5\text{H}_{11})_4\text{N}^+$ ;  $\text{Ph}_4\text{P}^+ = (\text{C}_6\text{H}_5)_4\text{P}^+$ ;  $\text{Ph}_4\text{As}^+ = (\text{C}_6\text{H}_5)_4\text{As}^+$ ;  $\text{BPh}_4^- = \text{B}(\text{C}_6\text{H}_5)_4^-$ .

#### References

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## TABLES OF SELECTED DATA

$\Delta H_{\text{f}}^{\circ}(X, W \rightarrow S)$  / kJ/mol (upper values for each ion), and  
 $\Delta S_{\text{f}}^{\circ}(X, W \rightarrow S)$  / J/K·mol (mol/dm<sup>3</sup> scale) (lower values); 298.15K

Solvent*	D <sub>2</sub> O	MeOH	EtOH	PrOH	PC	NH <sub>3</sub> **
H <sup>+</sup>					44	
Li <sup>+</sup>	1.9	-21.7 -83	-20.2 -101	-100	2.8 -65	-45
Na <sup>+</sup>	2.6	-20.7 -95	-19.4 -108	-106	-10.5 -75	-36
K <sup>+</sup>	2.8	-19.0 -94	-19.6 -113	-121	-22.5 -89	-26
Rb <sup>+</sup>	2.9	-16.5 -85	-103	-118	-24.9 -77	-25
Cs <sup>+</sup>	3.0	-14.1 -76	-92	-104	-27.5 -66	-33
Ag <sup>+</sup>	2.3	-20.9 -95			-11.1 -92	-106
Ca <sup>++</sup>	5.4					-98
Sr <sup>++</sup>	5.7					-109
Ba <sup>++</sup>	6.1	-60.6				-102
NH <sub>4</sub> <sup>+</sup>	1.3				-19.8	
Me <sub>4</sub> N <sup>+</sup>	1.8	0.3 -18	0.2 -36	(-45)	-18	
Et <sub>4</sub> N <sup>+</sup>	0.9	7.1 [31]				
Pr <sub>4</sub> N <sup>+</sup>	-0.2	15				
Bu <sub>4</sub> N <sup>+</sup>	-1.0	20 142			21	
Ph <sub>4</sub> As <sup>+</sup>	0.7	-1.0 74		90	-13.1 71	
F <sup>-</sup>	-2.6					
Cl <sup>-</sup>	-0.2	8.4 -17	10.4 -33	-58	26.2 -43	6
Br <sup>-</sup>	0.4	4.5 -23	5.5 -43	-65	15.2 -51	-16
I <sup>-</sup>	1.0	-1.0 -31	-0.7 -46	-70	-1.6 -64	-29
N <sub>3</sub> <sup>-</sup>		0.5 -34			16.7 -43	
ClO <sub>4</sub> <sup>-</sup>	-0.2	-3.1 -26	-2.7 -46	-62	-16.3	
BPh <sub>4</sub> <sup>-</sup>	0.7	-0.9 74		90	-13.2 71	

\*See list of solvents for the names corresponding to the abbreviations. \*\*At 240 K.

## TABLES OF SELECTED DATA (contd.)

$\Delta H_{\ddagger}^{\circ}(X, W+S)$  / kJ/mol (upper values for each ion), and  
 $\Delta S_{\ddagger}^{\circ}(X, W+S)$  / J/K·mol (mol/dm<sup>3</sup> scale)(lower values); 298.15 K.

Solvent*	FA	DMF	NMPy	MeCN	DMSO	TMS**
H <sup>+</sup>						73
Li <sup>+</sup>	-6.0 13	-25.4 [-60] -46			-27.1 -43	
Na <sup>+</sup>	-16.5 -29	-32.4 [-81] -67	-41	-13.3 -90	-29.2 -56	-16
K <sup>+</sup>	-17.9 -41	-35.7 [1100] -86	-47	-22.9 -103	-35.4 -84	-26
Rb <sup>+</sup>	-17.8 -41	-36.1 [-96] -82		-24.6 -103	-35 -87	-28
Cs <sup>+</sup>	-17.7 -38	-34.6 [-92] -78		-100	-33.0 -74	-26
Ag <sup>+</sup>		-35 [-77] -63		-52.7 -100	-53.3 [-89]	-14
Ca <sup>++</sup>						
Sr <sup>++</sup>						
Ba <sup>++</sup>					-80	
NH <sub>4</sub> <sup>+</sup>					-41	
Me <sub>4</sub> N <sup>+</sup>		-13 [-33] -19		-15.3 [-41]	-16.4 [-24]	
Et <sub>4</sub> N <sup>+</sup>		[31] 45		39		
Pr <sub>4</sub> N <sup>+</sup>						
Bu <sub>4</sub> N <sup>+</sup>		[151] 165				
Ph <sub>4</sub> As <sup>+</sup>	-0.5 80	-17.2 [68] 82	-17	-11.1 75	-10.6 85	-11
F <sup>-</sup>	19.9					
Cl <sup>-</sup>	3.5 -32	17.9 [-85] -99	27	19.3 -74	20.0 -62	27
Br <sup>-</sup>	-1.5 -39	0.6 [-92] -106	13	8.0 -76	4.6 -81	13
I <sup>-</sup>	-6.8 -47	-15.0 [-105] -119	2	-7.6 -85	-11.5 [-86]	-8
N <sub>3</sub> <sup>-</sup>		[-111] -125		8.8 [-72]	-92	15
ClO <sub>4</sub> <sup>-</sup>	-40	-23.4 [-86] -100	-11	-72	-18.2 -69	
BPh <sub>4</sub> <sup>-</sup>	-0.5 80	-17.2 [68] 82	-17	-10.4 75	-11.0 85	-11

\*See list of solvents for the names corresponding to the abbreviations. \*\*At 303.15 K.

**Solvent, S = Deuterium oxide**

$\Delta H_t^\circ(X, W \rightarrow S)$  / kJ/mol, mol/dm<sup>3</sup> scale, 298.15 K, ref. 1.  
 $\Delta S_t^\circ(X, W \rightarrow S)$  / J/K.mol, mol/dm<sup>3</sup> scale, 298.15 K, ref. 2.

ref.	1	1	2		
wt.	1.0	1.0	0		
Li <sup>+</sup>	1.88	F <sup>-</sup>	-2.55	Li <sup>+</sup>	4.2
Na <sup>+</sup>	2.55	Cl <sup>-</sup>	-0.21	Na <sup>+</sup>	4.2
K <sup>+</sup>	2.76	Br <sup>-</sup>	0.38	K <sup>+</sup>	4.6
Rb <sup>+</sup>	2.85	I <sup>-</sup>	0.96	Cs <sup>+</sup>	5.8
Cs <sup>+</sup>	2.97	CN <sup>-</sup>	-0.67	F <sup>-</sup>	-0.4
Ag <sup>+</sup>	2.26	NO <sub>3</sub> <sup>-</sup>	-0.50	Cl <sup>-</sup>	4.6
Mg <sup>++</sup>	4.06	ClO <sub>4</sub> <sup>-</sup>	-0.17	Br <sup>-</sup>	5.9
Ca <sup>++</sup>	5.44	HCO <sub>2</sub> <sup>-</sup>	-1.76	I <sup>-</sup>	6.0
Sr <sup>++</sup>	5.73	CH <sub>3</sub> CO <sub>2</sub> <sup>-</sup>	-2.26		
Ba <sup>++</sup>	6.11	CO <sub>3</sub> <sup>2-</sup>	-3.35		
Hg <sup>++</sup>	-0.50	SO <sub>4</sub> <sup>2-</sup>	-2.64		
NH <sub>4</sub> <sup>+</sup>	1.26	BPh <sub>4</sub> <sup>-</sup>	0.67		
Me <sub>4</sub> N <sup>+</sup>	1.80				
Et <sub>4</sub> N <sup>+</sup>	0.88				
Pr <sub>4</sub> N <sup>+</sup>	-0.21				
Bu <sub>4</sub> N <sup>+</sup>	-0.96				
Pn <sub>4</sub> N <sup>+</sup>	-1.59				
Ph <sub>4</sub> P <sup>+</sup>	0.71				
Ph <sub>4</sub> As <sup>+</sup>	0.67				

Deuterium Oxide - Reference and Comments

1. H.L. Friedman and C.V. Krishnan, in F. Franks, ed., Water. A Comprehensive Treatise, Plenum, New York, Vol. 3, 1973, p. 90; Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
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**Solvent, S = Methanol**

$\Delta H_t^\circ(X, W \rightarrow S)$  / kJ/mol, mol/dm<sup>3</sup> scale, 298.15 K

ref.*	1	2	3	4	5	6	7	8	9
wt.	1.0	1.0	0.1	0.2	0.5	1.0	1.0	1.0	0.5
Li <sup>+</sup>	-15.5	-22.2	-14.6		-22.2	-21.8	-22.2	-22.2	-22
Na <sup>+</sup>	-20.1	120.6	-18.4		-20.6	-20.5	-20.5	-20.6	-24
K <sup>+</sup>	-19.7	-18.9	-17.2		-18.9	-18.4	-18.4	-18.9	-22
Rb <sup>+</sup>	-19.7	-15.6	-12.1		-15.5	-15.1	-15.5		-19
Cs <sup>+</sup>	-15.9	-13.7	-10.5		-14.7	-13.4	-13.8	-13.7	-15
Ag <sup>+</sup>				-21.3		-20.9	-20.9		
Me <sub>4</sub> N <sup>+</sup>	-0.2	1.1	4.2		1.2	1.7		1.2	
Et <sub>4</sub> N <sup>+</sup>		9.1	10.5						
Pr <sub>4</sub> N <sup>+</sup>		16.0	30.5						
Bu <sub>4</sub> N <sup>+</sup>		20.6							
Ph <sub>4</sub> As <sup>+</sup>	3.3	-1.8			-1.7	-1.7	-1.7	-1.8	
F <sup>-</sup>									5
Cl <sup>-</sup>	7.9	(-0.8)	4.2		8.4	8.4	8.4	8.4	10
Br <sup>-</sup>	3.8	4.6	1.3	9.6	4.6	3.8	4.6	4.6	6
I <sup>-</sup>	-1.7	-2.0	-5.4		-2.0	-2.1	-2.1	-2.0	0
SCN <sup>-</sup>							-3.2		
N <sub>3</sub> <sup>-</sup>						0.4	0.4		
ClO <sub>4</sub> <sup>-</sup>	-4.6	-2.5	-6.7		-2.4	-2.5	-2.5	-2.4	
CF <sub>3</sub> CO <sub>2</sub> <sup>-</sup>		9.2							
BPh <sub>4</sub> <sup>-</sup>	3.3	-1.8	22.2		-1.8	-1.7	-1.7	-1.8	

\*References are printed at the top of the facing page

$\Delta H_t^\circ$  Methanol - References and Comments

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- J.F. Coetzee and E.J. Subak, Jr., Rev. Chim. Min., 15, 40 (1979); from  $\Delta H_t^\circ(\text{ClO}_4^-, \text{W} \rightarrow \text{S})$  from ref. 3.

## Solvent, S = Methanol (contd.)

 $\Delta H_t^\circ(\text{X}, \text{W} \rightarrow \text{S})$  / kJ/mol, mol/dm<sup>3</sup> scale, 298.15 K.

ref.*	10	11	12	13	14	15	16	
wt.	0.1	1.0	1.0	1.0	0.5	1.0	1.0	selected
Li <sup>+</sup>			-22.2	-21.7	-25.0	-22.2		-21.7
Na <sup>+</sup>			-20.5	-20.4	-23.7	-20.6		-20.7
K <sup>+</sup>			-18.4	-18.3	-22.2	-18.9		-19.0
Rb <sup>+</sup>			-15.5	-16.4	-18.9	-15.5		-16.5
Cs <sup>+</sup>			-13.8	-14.1	-15.5	-13.7		-14.1
Ag <sup>+</sup>			-20.9			-20.9		-20.9
Ba <sup>++</sup>		-59.2	-59.2				-61.9	-60.6
Mn <sup>++</sup>							-38.9	
Ni <sup>++</sup>							-71.5	
Zn <sup>++</sup>		-45.6	-45.6					
Cd <sup>++</sup>		-40.4	-40.4					
NH <sub>4</sub> <sup>+</sup>						-18.8		
Me <sub>4</sub> N <sup>+</sup>				-3.0		1.2		0.3
Et <sub>4</sub> N <sup>+</sup>				4.8		9.1		7.1
Pr <sub>4</sub> N <sup>+</sup>				12.2		16.0		15
Bu <sub>4</sub> N <sup>+</sup>				17.9		20.6		20
Ph <sub>4</sub> As <sup>+</sup>				-1.7		-1.8		-1.0
Cl <sup>-</sup>				8.3	(8.4)	8.4		8.4
Br <sup>-</sup>				4.1	5.5	4.6		4.5
I <sup>-</sup>				1.6	-1.7	-2.0		-2.0
SCN <sup>-</sup>								
N <sub>3</sub> <sup>-</sup>	0.8					0.4		0.5
ClO <sub>4</sub> <sup>-</sup>				-4.3		-2.4		-3.1
NO <sub>3</sub> <sup>-</sup>						4.2		
CF <sub>3</sub> SO <sub>3</sub> <sup>-</sup>			4.4					-1.0
BPh <sub>4</sub> <sup>-</sup>				-1.7				

\*References are printed at the top of this page

Solvent, S = Methanol (contd.)  $\Delta S_f^\ddagger(X, W+S) / J/K.mol$ , mol/dm<sup>3</sup> scale, 298.15 K

ref.	1	2	3	4	5	6	7	8	ref.	9	10	11	12	13	14	selected
wt.	0.5	1.0	0.2	0.5	1.0	1.0	1.0	0.2	wt.	0.2	0.2	1.0	1.0	0.5	1.0	
H <sup>+</sup>									H <sup>+</sup>	-45						
Li <sup>+</sup>	-62			-86	-94	-87	-89		Li <sup>+</sup>	-41		-87	-82	-94	-87	-83
Na <sup>+</sup>	-91			-97	-97	-97	-87		Na <sup>+</sup>	-57		-97	-96	-107	-98	-95
K <sup>+</sup>	-95	-95		-97	-95	-95	-95	-85	K <sup>+</sup>	-66		-95	-95	-108	-96	-94
Rb <sup>+</sup>	-83	-83		-87	-84	-86	-87	-92	Rb <sup>+</sup>	-64		-86	-90	-99	-87	-85
Cs <sup>+</sup>	-74	-77		-81	-77	-72	-78	-87	Cs <sup>+</sup>	-64		-72	-77	-77	-77	-76
Ag <sup>+</sup>			-100		-95	-95	-95		Ag <sup>+</sup>			-95	-94		-95	-95
NH <sub>4</sub> <sup>+</sup>		-15					-80		Ba <sup>2+</sup>			-260				
Me <sub>4</sub> <sup>+</sup>	34	33		-20			-20	-22	Zn <sup>2+</sup>			-245				
Et <sub>4</sub> <sup>+</sup>									Cd <sup>2+</sup>			-246				
Pr <sub>4</sub> <sup>+</sup>									NH <sub>4</sub> <sup>+</sup>						-79	
Bu <sub>4</sub> <sup>+</sup>	147	139							Me <sub>4</sub> N <sup>+</sup>				-18		-20	-18
Ph <sub>4</sub> As <sup>+</sup>		77		72	73	73	72		Et <sub>4</sub> N <sup>+</sup>			28	28	27	27	[31]
Cl <sup>-</sup>	-30	-8		-16	-14	-14	-16	-12	Pr <sub>4</sub> N <sup>+</sup>			83	83	82	82	142
Br <sup>-</sup>	-34	-13	0	-21	-25	-23	-21	-21	Bu <sub>4</sub> N <sup>+</sup>						72	74
I <sup>-</sup>	-43	-21		-29	-30	-30	-29	-25	Ph <sub>4</sub> As <sup>+</sup>			74	74		-16	-17
SCN <sup>-</sup>									Cl <sup>-</sup>				-18	(-17)	-16	-17
N <sub>3</sub> <sup>-</sup>									Br <sup>-</sup>				-24	-21	-21	-33
ClO <sub>4</sub> <sup>-</sup>	-34	-21		-29	-32	-36	-35	-26	I <sup>-</sup>				-32	-31	-29	-31
BPh <sub>4</sub> <sup>-</sup>	122	77		72	73	73	72		N <sub>3</sub> <sup>-</sup>		-24				-35	
									NO <sub>3</sub> <sup>-</sup>				-20		-28	-26
									ClO <sub>4</sub> <sup>-</sup>				74		72	74
									BPh <sub>4</sub> <sup>-</sup>							

 $\Delta S_f^\ddagger$  Methanol - References and Comments

1. D. Bax, C.L. Deligny, and M. Alfenaar, *Rec. Trav. Chim.*, **91**, 452 (1972); extrapolation method.
2. M.H. Abraham, *J. Chem. Soc. Chem. Comm.*, **1972**, 888; assumption that  $\Delta S_f^\ddagger(\text{Me}_4\text{N}^+, \text{W+S}) = 0$ .
3. B.G. Cox and A.J. Parker, *J. Am. Chem. Soc.*, **95**, 402 (1973); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
4. M.H. Abraham, *J. Chem. Soc.*, **1973**, 1375 (1973); from correspondence plot.
5. B.G. Cox, *Ann. Rev. Chem. Soc.*, **70**, 249 (1973); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
6. B.G. Cox, G.R. Hedwig, A.J. Parker, and D.W. Watts, *Austr. J. Chem.*, **27**, 477 (1974); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
7. M.H. Abraham and A.F. Danil de Namor, *J. Chem. Soc., Faraday Trans. 1*, **74**, 2101 (1978); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption, also from correspondence plot, which yields values more positive by 29 J K<sup>-1</sup>mol<sup>-1</sup>.
8. M.H. Abraham and J. Liszi, *J. Chem. Soc., Faraday Trans. 1*, **74**, 2858 (1978); electrostatic calculation.
9. C.M. Criss, R.P. Held, and E. Luksha, *J. Phys. Chem.*, **72**, 2970 (1968); correspondence method (linear dependence on aqueous entropies).
10. B.G. Cox and A.J. Parker, *J. Am. Chem. Soc.*, **95**, 408 (1973); for N<sub>3</sub><sup>-</sup> Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
11. G.R. Hedwig, D.A. Owensby, and A.J. Parker, *J. Am. Chem. Soc.*, **97**, 3888 (1975); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
12. B.G. Cox and W.E. Waghorne, *Chem. Soc. Rev.*, **9**, 381 (1980); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
13. E. DeValera, D. Feakins, and W.E. Waghorne, *J. Chem. Soc. Faraday Trans. 1*, **76**, 560 (1980); using  $\Delta S_f^\ddagger(\text{Cl}^-, \text{H}_2\text{O} \rightarrow \text{MeOH}) = -17 \text{ J/K.mol}$ .
14. M.H. Abraham, A.F. Danil de Namor, and R.A. Schulz, *J. Chem. Soc. Faraday Trans. 1*, **76**, 869 (1980); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.



## Solvent, S = Ethanol

$\Delta H_{\text{t}}^{\circ}(X, W+S) / \text{kJ/mol, mol/dm}^3$ scale, 298.15 K.					$\Delta S_{\text{t}}^{\circ}(X, W+S) / \text{J/K}\cdot\text{mol, mol/dm}^3$ scale, 298.15 K						
ref.	1	2	3	selected	ref.	4	1a	2	5	6	selected
wt.	0.5	1.0	1.0		wt.	0.5	0.5	0.2	1.0	0.5	
Li <sup>+</sup>		-23.0	-17.4	-20.2	H <sup>+</sup>	-116					
Na <sup>+</sup>	-15.7	-24.3	-16.4	-19.4	Li <sup>+</sup>	-114		-101	-94		-101
K <sup>+</sup>	-16.8	-23.8	-17.2	-19.6	Na <sup>+</sup>	-131	-88	-128	-108	-95	-108
Cs <sup>+</sup>			-11.8		K <sup>+</sup>	-141	-88	-132	-111	-107	-113
NH <sub>4</sub> <sup>+</sup>			-26.5		Rb <sup>+</sup>				-103	-103	-103
Me <sub>4</sub> N <sup>+</sup>	0.2	(0)	0.2	0.2	Cs <sup>+</sup>				-90	-97	-92
Et <sub>4</sub> N <sup>+</sup>	10.7				NH <sub>4</sub> <sup>+</sup>				-111		
Ph <sub>4</sub> As <sup>+</sup>			0.0		Me <sub>4</sub> N <sup>+</sup>		-29	-40	-40	-32	-36
Cl <sup>-</sup>		10.5	10.2	10.4	Et <sub>4</sub> N <sup>+</sup>		46				
Br <sup>-</sup>	4.8	5.9	5.4	5.5	Ph <sub>4</sub> As <sup>+</sup>					69	
I <sup>-</sup>	-1.9	-0.4	-0.4	-0.7	Cl <sup>-</sup>	-35		-31	-33	-33	-33
ClO <sub>4</sub> <sup>-</sup>	-2.7		-2.6	-2.7	Br <sup>-</sup>	-41	-54	-40	-39	-41	-43
BPh <sub>4</sub> <sup>-</sup>			0.0		I <sup>-</sup>	-44	-59	-44	-41	-45	-46
					ClO <sub>4</sub> <sup>-</sup>		-54		-42	-47	-46
					BPh <sub>4</sub> <sup>-</sup>				68		

## Ethanol - References and Comments

- D. Bax, C.L. DeLigny, and A.G. Remijnse, *Rec. Trav. Chim.*, **91**, 965 (1972); extrapolation method, adjusted by adding -(+) 2.7 kJ/mol to cation (anion) values; extrapolation method.
- M.H. Abraham, E. Ah-Sing, A.F. Danil de Namor, T. Hill, A. Nasehzadeh, and R.A. Schulz, *J. Chem. Soc., Faraday Trans. 1*, **74**, 359 (1978); Ph<sub>4</sub>AsBPh<sub>4</sub>.
- M.H. Abraham, E. Ah-Sing, A.F. Danil de Namor, T. Hill, A. Nasehzadeh, and R.A. Schulz, *J. Chem. Soc., Faraday Trans. 2*, **74**, 359 (1978); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
- C.M. Criss, R.P. Held, and E. Luksha, *J. Phys. Chem.*, **72**, 2970 (1968); correspondence method (linear dependence on aqueous entropies).
- M.H. Abraham and A.F. Danil de Namor, *J. Chem. Soc., Faraday Trans. 1*, **74**, 2101 (1978); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption, also from correspondence plot, which yields values more positive by 29 J K<sup>-1</sup>mol<sup>-1</sup>.
- M.H. Abraham and J. Liszi, *J. Chem. Soc., Faraday Trans. 1*, **74**, 2858 (1978); electrostatic calculation.

## Solvent, S = 1-Propanol

$\Delta H_{\text{t}}^{\circ}(X, W+S) / \text{kJ/mol, mol/dm}^3$ scale, 298.15 K			$\Delta S_{\text{t}}^{\circ}(X, W+S) / \text{J/K}\cdot\text{mol, mol/dm}^3$ scale, 298 K			
ref.	1	2	ref.	3	4	selected
wt.	1.0	1.0	wt.	1.0	0.5	
Li <sup>+</sup>	-18.2	-18.6	Li <sup>+</sup>	-100		-100
Na <sup>+</sup>	-18.8	-18.8	Na <sup>+</sup>	-105	-108	-106
K <sup>+</sup>	-18.3	-18.3	K <sup>+</sup>	-121	-121	-121
Cs <sup>+</sup>	-12.7	-12.7	Rb <sup>+</sup>	-118	-116	-118
Mg <sup>++</sup>		-10.0	Cs <sup>+</sup>	-101	-110	-104
Ca <sup>++</sup>		-10.9	NH <sub>4</sub> <sup>+</sup>	-118		-118
Sr <sup>++</sup>		-15.1	Me <sub>4</sub> N <sup>+</sup>		-45	(-45)
Ba <sup>++</sup>		-21.8	Ph <sub>4</sub> As <sup>+</sup>	90		90
Pb <sup>++</sup>		-26.4	Cl <sup>-</sup>	-58	-58	-58
NH <sub>4</sub> <sup>+</sup>		-28.0	Br <sup>-</sup>	-65	-66	-65
Et <sub>4</sub> N <sup>+</sup>		9.6	I <sup>-</sup>	-70	-70	-70
Bu <sub>4</sub> N <sup>+</sup>		21.3	ClO <sub>4</sub> <sup>-</sup>	-58	-71	-62
Ph <sub>4</sub> As <sup>+</sup>	1.5	1.5	BPh <sub>4</sub> <sup>-</sup>	90		90
Cl <sup>-</sup>	8.4	8.4				
Br <sup>-</sup>	2.5	2.5				
I <sup>-</sup>	-1.4	-1.5				
ClO <sub>4</sub> <sup>-</sup>	0.0	0.0				
BPh <sub>4</sub> <sup>-</sup>	1.5	1.5				

## 1-Propanol - References and Comments

- M.H. Abraham, E. Ah-Sing, A.F. Danil de Namor, T. Hill, A. Nasehzadeh, and R.A. Schulz, *J. Chem. Soc., Faraday Trans. 1*, **74**, 359 (1978); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
- M.H. Abraham, A.F. Danil de Namor, and R.A. Schulz, *J. Soln. Chem.*, **6**, 491 (1977); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
- M.H. Abraham and A.F. Danil de Namor, *J. Chem. Soc., Faraday Trans. 1*, **74**, 2101 (1978); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption, also from correspondence plot, which yields values more positive by 29 J K<sup>-1</sup>mol<sup>-1</sup>.
- M.H. Abraham and J. Liszi, *J. Chem. Soc., Faraday Trans. 1*, **74**, 2858 (1978); electrostatic calculation.

<b>Solvent, S = 1,2-Dimethoxyethane</b>		<b>Solvent, S = Tetrahydrofuran</b>	
$\Delta S_{\ddagger}^{\circ}(X, W \rightarrow S) / \text{J/K.mol, mol/dm}^3$ scale, 298.15 K		$\Delta S_{\ddagger}^{\circ}(X, W \rightarrow S) / \text{J/K.mol, mol/dm}^3$ scale, 298.15 K	
ref.	1	ref.	1
wt.	0	wt.	0
Na <sup>+</sup>	-103	Na <sup>+</sup>	-202
K <sup>+</sup>	-204	K <sup>+</sup>	-173
Rb <sup>+</sup>	-341	Rb <sup>+</sup>	-197
Cs <sup>+</sup>	-277	Cs <sup>+</sup>	-275
Cl <sup>-</sup>	-223	Cl <sup>-</sup>	-179

#### References and Comments

1. M.H. Abraham and J. Liszi, J. Chem. Soc., Faraday Trans. 1, 74, 2858 (1978); electrostatic calculation.

#### Solvent, S = Acetone

$\Delta S_{\ddagger}^{\circ}(X, W \rightarrow S) / \text{J/K.mol, mol/dm}^3$   
scale, 298.15 K

ref.	1	2
wt.	0	0
Na <sup>+</sup>	-84	-109
K <sup>+</sup>	-75	-122
Rb <sup>+</sup>		-117
Cs <sup>+</sup>		-111
Me <sub>4</sub> N <sup>+</sup>	(0)	-46
Cl <sup>-</sup>	-163	-107
Br <sup>-</sup>	-167	-115
I <sup>-</sup>		-119
ClO <sub>4</sub> <sup>-</sup>		-121
BPh <sub>4</sub> <sup>-</sup>	17	

#### $\Delta S_{\ddagger}^{\circ}$ Acetone - References and Comments

1. M.H. Abraham, J. Chem. Soc., Faraday Trans. 1, 69, 1375 (1973); from correspondence plot.
2. M.H. Abraham and J. Liszi, J. Chem. Soc., Faraday Trans. 1, 74, 2858 (1978); electrostatic calculation.

**Solvent, S = Propylene carbonate**  $\Delta H_{tr}^{\circ}(X, W+S)$  / kJ/mol, mol/dm<sup>3</sup> scale, 298.15 K

ref.	1	2	3	4	5	6	7	8	ref.	9	10	11	12	13	14	selec-
wt.	0.5	1.0	1.0	0.5	1.0	1.0	0.5	0.5	wt.	0.5	0.2	1.0	1.0	1.0	1.0	ted
H <sup>+</sup>							43.9	44.0	H <sup>+</sup>							44
Li <sup>+</sup>	-0.2	3.1			1.7	3.8			Li <sup>+</sup>	3.2		5.8		2.5		2.8
Na <sup>+</sup>	-13.8	-10.2			-8.8	-6.7			Na <sup>+</sup>	-10.2		-12.2		-11.3		-10.5
K <sup>+</sup>	-25.1	-21.9			-20.9	-20.9		-25.1	K <sup>+</sup>	-21.7				-23.0		-22.5
Rb <sup>+</sup>	-28.0	-24.8			-23.4	-23.4			Rb <sup>+</sup>	-24.4				-25.5		-24.9
Cs <sup>+</sup>	-31.0	-26.8			-25.9	-25.9			Cs <sup>+</sup>	-27.3				-28.0		-27.5
Ag <sup>+</sup>				-16.7	-12.6	-12.6			Ag <sup>+</sup>			-7.2		-9.2		-11.1
NH <sub>4</sub> <sup>+</sup>					-19.2			-20.9	NH <sub>4</sub> <sup>+</sup>				13.8			
Me <sub>4</sub> N <sup>+</sup>	-20.1	-16.3							NH <sub>4</sub> <sup>+</sup>							-19.8
Ph <sub>4</sub> As <sup>+</sup>	-10.9	-14.6			-15.1	-15.1			Me <sub>4</sub> N <sup>+</sup>					-17.6		-18
Cl <sup>-</sup>	27.6	31.2	17.2		28.0	28.0	28.0		Et <sub>4</sub> N <sup>+</sup>					-0.4		
Br <sup>-</sup>	(18.0)	18.2	13.6	18.4	17.6	17.6			Pr <sub>4</sub> N <sup>+</sup>					10.5		
I <sup>-</sup>	-2.7	0.4	-3.3		-0.8	-0.8			Bu <sub>4</sub> N <sup>+</sup>					18.8	21.9	21
N <sub>3</sub> <sup>-</sup>					16.3	16.3			Ph <sub>4</sub> As <sup>+</sup>					-13.4		-13.1
ClO <sub>4</sub> <sup>-</sup>	-14.6	-12.8	-16.4		-15.5	-15.5			Cl <sup>-</sup>					25.1		26.2
BPh <sub>4</sub> <sup>-</sup>		-10.9	-14.6		-15.1	-15.1			Br <sup>-</sup>					13.4	7.4	15.2
									I <sup>-</sup>	-3.3				-2.1		-1.6
									N <sub>3</sub> <sup>-</sup>		20.5					16.7
									ClO <sub>4</sub> <sup>-</sup>	-16.4				-15.5	-23.0	-16.3
									CF <sub>3</sub> CO <sub>2</sub> <sup>-</sup>						21.9	
									BBu <sub>4</sub> <sup>-</sup>	32.7						
									BPh <sub>4</sub> <sup>-</sup>	(-14.6)		-9.3		-13.4		

 $\Delta H_{tr}^{\circ}$  Propylene Carbonate - References

- M. Salomon, *J. Phys. Chem.*, **73**, 3299 (1969); values relative to  $\Delta H_{tr}^{\circ}(\text{Br}^-, W+S) = 0$ , adjusted by addition of 18 kJ/mol to anion values.
- H. Choux and R.L. Benoit, *J. Am. Chem. Soc.*, **91**, 6221 (1969); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
- C.V. Krishnan and H.L. Friedman, *J. Phys. Chem.*, **73**, 3934 (1969); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
- B.G. Cox and A.J. Parker, *J. Am. Chem. Soc.*, **95**, 402 (1973); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
- B.G. Cox, *Ann. Rev. Chem. Soc.*, **70**, 249 (1973); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
- B.G. Cox, G.R. Hedwig, A.J. Parker, and D.W. Watts, *Austr. J. Chem.*, **27**, 477 (1974); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
- R. Domain, M. Rinfret, and R.L. Benoit, *Can. J. Chem.*, **54**, 2101 (1976); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
- E. Milanova, S.Y. Lam, B. Desjardins, and R.L. Benoit, *Adv. Chem. Ser.*, **177**, 145 (1979); the extrathermodynamic assumption is not stated.
- Y.-C. Wu and H.L. Friedman, *J. Phys. Chem.*, **70**, 501 (1966); using transfer data for BPh<sub>4</sub><sup>-</sup> from C.V. Krishnan and H.L. Friedman, *ibid.*, **73**, 3934 (1969); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
- B.G. Cox and A.J. Parker, *J. Am. Chem. Soc.*, **95**, 408 (1973); for N<sub>3</sub><sup>-</sup> Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
- B.G. Cox, W.E. Waghorne, and C.K. Pigott, *J. Chem. Soc., Faraday Trans. 1*, **75**, 227 (1979); using transfer data from W to DMSO from B.G. Cox, *Ann. Rev. Chem. Soc.*, **70**, 249 (1973); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
- J.F. Coetzee and E.J. Subak, Jr., *Rev. Chim. Min.*, **15**, 40 (1979); from  $\Delta H_{tr}^{\circ}(X, W+S)$  data from ref. 6.
- B.G. Cox and W.E. Waghorne, *Chem. Soc. Rev.*, **9**, 391 (1980); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
- Y. Kondo, K. Yuki, T. Yoshida, and N. Tokura, *J. Chem. Soc., Faraday Trans. 1*, **76**, 812 (1980); Bu<sub>4</sub>NBBu<sub>4</sub> assumption.

**Solvent, S = Propylene carbonate (contd.)** $\Delta S_{\ddagger}^{\circ}(X, W \rightarrow S) / J/K.mol/dm^3$  scale, 298.15 K

ref.	1	2	3	4	5	6	selected
wt.	0.5	1.0	1.0	0.5	1.0	1.0	
Li <sup>+</sup>		-69	-67		-67	-54	-65
Na <sup>+</sup>		-66	-73		-80	-79	-75
K <sup>+</sup>		-81	-90		-92	-91	-89
Rb <sup>+</sup>		-60	-69		-88	-91	-77
Cs <sup>+</sup>		-38	-46		-85	-93	-66
Ag <sup>+</sup>	-95	-88	-95		-93	-89	-92
Me <sub>4</sub> N <sup>+</sup>					-17		
Et <sub>4</sub> N <sup>+</sup>					46		
Pr <sub>4</sub> N <sup>+</sup>					112		
Bu <sub>4</sub> N <sup>+</sup>					167		
Ph <sub>4</sub> As <sup>+</sup>		69	69		70	76	71
Cl <sup>-</sup>		-48	-32		-46	-46	-43
Br <sup>-</sup>	-56	-51	-40		-54	-57	-51
I <sup>-</sup>		-67	-62		-59	-67	[-64]
N <sub>3</sub> <sup>-</sup>		-45	-42	-39			-43
ClO <sub>4</sub> <sup>-</sup>					-58		
BPh <sub>4</sub> <sup>-</sup>		69	69		70	76	71

 $\Delta S_{\ddagger}^{\circ}$  Propylene carbonate - References and Comments

1. B.G. Cox and A.J. Parker, *J. Am. Chem. Soc.*, **95**, 402 (1973); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
2. B.G. Cox, *Ann. Rev. Chem. Soc.*, **70**, 249 (1973); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
3. B.G. Cox, G.R. Hedwig, A.J. Parker, and D.W. Watts, *Austr. J. Chem.*, **27**, 477 (1974); Ph<sub>4</sub>AsBP<sub>4</sub> assumption.
4. B.G. Cox and A.J. Parker, *J. Am. Chem. Soc.*, **95**, 408 (1973); for N<sub>3</sub><sup>-</sup> Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
5. M. Abraham, *Monatsh. Chem.*, **110**, 517 (1979); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
6. B.G. Cox and W.E. Waghorne, *Chem. Soc. Rev.*, **9**, 381 (1980); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.

**Solvent, S = Pyridine** $\Delta H_{\ddagger}^{\circ}(X, W \rightarrow S) / kJ/mol, mol/dm^3$  scale, 298.15 K

ref.	1	ref.	1
wt.	1.0	wt.	1.0
Na <sup>+</sup>	-30.3	Cl <sup>-</sup>	28.2
Ag <sup>+</sup>	-106	Br <sup>-</sup>	10.9
Hg <sup>++</sup>	-160	I <sup>-</sup>	-7.3
Et <sub>4</sub> N <sup>+</sup>	-3.7	SCN <sup>-</sup>	-4.7
Bu <sub>4</sub> N <sup>+</sup>	7.9	ClO <sub>4</sub> <sup>-</sup>	-18.8
Ph <sub>4</sub> As <sup>+</sup>	-22.8	BPh <sub>4</sub> <sup>-</sup>	-22.8

Pyridine - References and Comments

1. S. Ahrland, S. Ishigura, and R. Portanova, *priv. commun.* (correction) and to be published; quoted in S. Ahrland, *Pure Appl. Chem.*, **54**, 1451 (1982); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.

**Solvent, S = Ammonia** $\Delta H_{\text{t}}^{\circ}(\text{X}, \text{W} \rightarrow \text{S}) / \text{kJ/mol}, \text{mol/dm}^3 \text{ scale}, 240 \text{ K}$ 

ref.	1	2	3	4	selected
wt.	0	1.0	0.5	1.0	
Li <sup>+</sup>	-131	-55		-42	-48
Na <sup>+</sup>	-152	-47	-35	-34	-39
K <sup>+</sup>	-130	-34	-38	-26	-32
Rb <sup>+</sup>	-132	-36	-26	-19	-27
Cs <sup>+</sup>		-44	-33	-20	-32
Ag <sup>+</sup>	-242	-116		-109	-113
Ca <sup>++</sup>	-321	-121		-104	-113
Sr <sup>++</sup>	-344	-131		-101	-116
Ba <sup>++</sup>	-365	-130		-95	-113
Hg <sup>++</sup>	-449	-252		-217	-235
Pb <sup>++</sup>		-179		-145	-162
F <sup>-</sup>			24		
Cl <sup>-</sup>	131	22	-9	2	6
Br <sup>-</sup>	109	-4	-15	-23	-14
I <sup>-</sup>	100	-17	-33	-20	-21

 $\Delta H_{\text{t}}^{\circ}$  ammonia - References and Comments

1. L.V. Coulter, J. Phys. Chem., 57, 553 (1953); electrostatic calculation.
2. W.L. Jolly, Progr. Inorg. Chem., 1, 235 (1959); from  $\Delta H_{\text{f}}^{\circ}$  of the ammoniated e<sup>-</sup>.
3. G. Somsen and L. Weeda, J. Electroanal. Chem. Interfac. Electrochem., 29, 375 (1971); electrostatic extrapolation, adjusted by adding +(-) 33 kJ/mol to cation (anion) values.
4. N.M. Senozan, J. Inorg. Nucl. Chem., 35, 727 (1973); relative to  $\Delta H_{\text{sol}}^{\circ}$  of Na<sup>+</sup> from Born equation.

**Solvent, S = Ammonia (contd.)** $\Delta S_{\text{t}}^{\circ}(\text{X}, \text{W} \rightarrow \text{S}) / \text{J/K.mol}, \text{mol/dm}^3 \text{ scale}, 240 \text{ K}$ 

ref.	1	2	ref.	1	2
wt.	0	0	wt.	0	0
H <sup>+</sup>	-100		Me <sub>4</sub> N <sup>+</sup>		-38
Li <sup>+</sup>	-81		Cl <sup>-</sup>	-90	-99
Na <sup>+</sup>	-97	-101	Br <sup>-</sup>	-115	-107
K <sup>+</sup>	-113	-114	I <sup>-</sup>	-122	-111
Rb <sup>+</sup>	-103	-109	ClO <sub>4</sub> <sup>-</sup>		-113
Cs <sup>+</sup>	-112	-103			

 $\Delta S_{\text{t}}^{\circ}$  Ammonia - References and Comments

1. C.M. Criss, R.P. Held, and E. Luksha, J. Phys. Chem., 72, 2970 (1968); correspondence method (linear dependence on aqueous entropies).
2. M.H. Abraham and J. Liszi, J. Chem. Soc., Faraday Trans. 1, 74, 2858 (1978); electrostatic calculation.

**Solvent, S = Formamide** $\Delta H_t^\circ(X, W+S) / \text{kJ/mol, mol/dm}^3 \text{ scale, 298.15 K}$ 

ref.	1	2	3	4	5	6	7	8	selected
wt.	0.5	0.5	0.5	0.2	1.0	1.0	1.0	1.0	
Li <sup>+</sup>	-5.7	-5.4	-9	-10	-5.4	-5.4		-5.5	-6.0
Na <sup>+</sup>	-16.2	-15.5	-18	-21.8	-16.3	-16.3		-15.9	-16.5
K <sup>+</sup>	-17.4	-16.7	-20	-19.7	-16.7	-16.7		-19.9	-17.9
Rb <sup>+</sup>	-17.4	-18.0	-19	-22.2	-17.2	-17.2		-17.6	-17.8
Cs <sup>+</sup>	-16.9	-18.8	-18	-20.9	-17.2	-17.2		-17.9	-17.7
Ag <sup>+</sup>					-22.6	-22.6			
Ba <sup>++</sup>							-40.2		
Zn <sup>++</sup>							-23.9		
Cd <sup>++</sup>							-27.5		
Me <sub>4</sub> N <sup>+</sup>					0.8			-2.1	
Et <sub>4</sub> N <sup>+</sup>								5.5	
Pr <sub>4</sub> N <sup>+</sup>								16.4	
Bu <sub>4</sub> N <sup>+</sup>								26.0	
Ph <sub>4</sub> As <sup>+</sup>					-0.4	-0.4	-0.4	-0.8	-0.5
F <sup>-</sup>	12.9	21.8	23					20.9	19.9
Cl <sup>-</sup>	3.6	2.9	5	5.0	3.3	3.3		3.3	3.5
Br <sup>-</sup>	-1.5	-1.7	0	1.7	-1.7	-1.7		-1.1	-1.5
I <sup>-</sup>	-7.3	-7.3	-5	0.4	-7.5	-7.5		-7.3	-6.8
SCN <sup>-</sup>						-10.9			
ClO <sub>3</sub> <sup>-</sup>							-2.9		
ClO <sub>4</sub> <sup>-</sup>					-20.1				
CF <sub>3</sub> CO <sub>2</sub> <sup>-</sup>							-1.5		
BPh <sub>4</sub> <sup>-</sup>					-0.4	-0.4	-0.4	-0.8	-0.5

 $\Delta H_t^\circ$  Formamide - References and Comments

1. G. Somsen and J. Coops, *Rec. Trav. Chim.*, **84**, 985 (1965); using  $\Delta H_t^\circ(\text{Rb}, \text{W} \rightarrow \text{FA}) = -17.4 \text{ kJ/mol}$  as the average from the literature that conforms to the Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
2. G. Somsen, *Rec. Trav. Chim.*, **85**, 526 (1966); electrostatic calculation and extrapolation.
3. G. Somsen and L. Weeda, *J. Electroanal. Chem. Interfac. Electrochem.*, **29**, 375 (1971); electrostatic extrapolation.
4. D.S. Gill, J.P. Singla, R.C. Paul, and S.P. Narula, *J. Chem. Soc., Dalton Trans.*, **1972**, 522; extrapolation method.
5. B.G. Cox, *Ann. Rev. Chem. Soc.*, **70**, 249 (1973); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
6. B.G. Cox, G.R. Hedwig, A.J. Parker, and D.W. Watts, *Austr. J. Chem.*, **27**, 477 (1974); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
7. G.R. Hedwig and A.J. Parker, *J. Am. Chem. Soc.*, **96**, 6589 (1974); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
8. B.G. Cox and W.E. Waghorne, *Chem. Soc. Rev.*, **9**, 381 (1980); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.

**Solvent, S = Formamide (contd.)** $\Delta S_t^\circ(X, W+S) / \text{J/K}\cdot\text{mol}, \text{mol}/\text{dm}^3 \text{ scale}, 298.15 \text{ K}$ 

ref.	1	2	3	4	5	select-
wt.	0.5	1.0	1.0	0.5	1.0	ted
H <sup>+</sup>	6					
Li <sup>+</sup>	11	14	14		11	13
Na <sup>+</sup>	-30	-23	-28	-29	-36	-29
K <sup>+</sup>	-36	-35	-35	-41	-55	-41
Rb <sup>+</sup>	-42	-39	-39	-36	-48	-41
Cs <sup>+</sup>	-42	-32	-32	-31	-53	-38
Ag <sup>+</sup>		-24	-24			
Me <sub>4</sub> N <sup>+</sup>				34	-16	
Pr <sub>4</sub> N <sup>+</sup>					89	
Ph <sub>4</sub> As <sup>+</sup>		79	79		81	80
F <sup>-</sup>	-4					
Cl <sup>-</sup>	-31	-35	-35	-26	-30	-32
Br <sup>-</sup>	-35	-44	-44	-35	-32	-39
I <sup>-</sup>	-40	-51	-51	-39	-47	-47
SCN <sup>-</sup>			-84			
ClO <sub>4</sub> <sup>-</sup>				-40	-40	-40
BPh <sub>4</sub> <sup>-</sup>		79	79		81	80

 $\Delta S_t^\circ$  Formamide - References and Comments

1. C.M. Criss, R.P. Held, and E. Luksha, *J. Phys. Chem.*, **72**, 2970 (1968); correspondence method (linear dependence on aqueous entropies).
2. B.G. Cox, *Ann. Rev. Chem. Soc.*, **70**, 249 (1973); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
3. B.G. Cox, G.R. Hedwig, A.J. Parker, and D.W. Watts, *Austr. J. Chem.*, **27**, 477 (1974); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
4. M.H. Abraham and J. Liszi, *J. Chem. Soc., Faraday Trans. 1*, **74**, 2858 (1978); electrostatic calculation.
5. B.G. Cox and W.E. Waghorne, *Chem. Soc. Rev.*, **9**, 381 (1980); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.

**Solvent, S = N-Methyl formamide** $\Delta H_t^\circ(X, W+S) / \text{kJ/mol}, \text{mol}/\text{dm}^3 \text{ scale}, 298.15 \text{ K}$ 

ref.	1	2	3	4
wt.	0	0	0	0
Li <sup>+</sup>	-31	-13.0	-21.3	-17.0
Na <sup>+</sup>	-32	-15.5	-22.4	-20.4
K <sup>+</sup>	-34	-21.8	-24.3	-26.0
Rb <sup>+</sup>	-37	-19.6	-22.4	-24.6
Cs <sup>+</sup>	-34	-19.2	-24.3	-22.6
Me <sub>4</sub> N <sup>+</sup>				(0)
F <sup>-</sup>	45	28.5		
Cl <sup>-</sup>	23	5.9	7.1	10.0
Br <sup>-</sup>	15	-1.7	1.7	2.6
I <sup>-</sup>	5	-12.1	0.4	-7.5
ClO <sub>4</sub> <sup>-</sup>				-19.8

 $\Delta H_t^\circ$  N-Methyl Formamide - References and Comments

1. G. Somsen and L. Weeda, *J. Electroanal. Chem. Interfac. Electrochem.*, **29**, 375 (1971); electrostatic extrapolation.
2. C.L. DeLigny, H.J.M. Denessen, and M. Alfenaar, *Rec. Trav. Chim.*, **90**, 1265 (1971); electrostatic calculation.
3. D.S. Gill, J.P. Singla, R.C. Paul, and S.P. Narula, *J. Chem. Soc., Dalton Trans.*, **1972**, 522; extrapolation method.
4. M.H. Abraham, *J. Chem. Soc., Faraday Trans. 1*, **69**, 1375 (1973); from correspondence plot.

**Solvent, S = N-Methyl formamide (contd.)** $\Delta S_t^\circ(X, W \rightarrow S) / J/K \cdot \text{mol}, \text{mol}/\text{dm}^3$  scale, 298.15 K

ref.	1	2	3	4
wt.	0	0	0	0
H <sup>+</sup>	-12			
Li <sup>+</sup>	-35	0	-42	
Na <sup>+</sup>	-28	-25	-50	-44
K <sup>+</sup>	-50	-46	-67	-57
Rb <sup>+</sup>		-42	-67	-52
Cs <sup>+</sup>	-54	-42	-59	-47
Me <sub>4</sub> N <sup>+</sup>			(0)	18
Cl <sup>-</sup>	-45	-50	-25	-42
Br <sup>-</sup>	-55	-46	-34	-51
I <sup>-</sup>				-55
ClO <sub>4</sub> <sup>-</sup>				-56

 $\Delta S_t^\circ$  N-Methyl Formamide - References and Comments

1. C.M. Criss, R.P. Held, and E. Luksha, *J. Phys. Chem.*, **72**, 2970 (1968); correspondence method (linear dependence on aqueous entropies).
2. C.L. DeLigny, H.J.M. Denessen, and M. Alfenaar, *Rec. Trav. Chim.*, **90**, 1265 (1971); electrostatic calculation.
3. M.H. Abraham, *J. Chem. Soc., Faraday Trans. 1*, **69**, 1375 (1973); from correspondence plot.
4. M.H. Abraham and J. Liszi, *J. Chem. Soc., Faraday Trans. 1*, **74**, 2858 (1978); electrostatic calculation.

<b>Solvent, S = N-Methyl acetamide</b>		<b>Solvent, S = N-Ethyl acetamide</b>	
$\Delta H_t^\circ(X, W \rightarrow S) / \text{kJ}/\text{mol}, \text{mol}/\text{dm}^3$ scale, 298.15 K		$\Delta H_t^\circ(X, W \rightarrow S) / \text{kJ}/\text{mol}, \text{mol}/\text{dm}^3$ scale, 298.15 K	
ref.	1	2	
wt.	0	1.0	
Li <sup>+</sup>	-30	-2.5	
Na <sup>+</sup>	-26	-18.8	
K <sup>+</sup>	-33	-32.6	
Rb <sup>+</sup>	-31		
Cs <sup>+</sup>	-28		
Ph <sub>4</sub> As <sup>+</sup>		28.5	
F <sup>-</sup>	-42		
Cl <sup>-</sup>	21	-2.5	
Br <sup>-</sup>	14	0.8	
I <sup>-</sup>	4	-0.4	
ClO <sub>4</sub> <sup>-</sup>		-1.3	
BPh <sub>4</sub> <sup>-</sup>		28.5	

References and Comments

1. G. Somsen and L. Weeda, *J. Electroanal. Chem. Interfac. Electrochem.*, **29**, 375 (1971); electrostatic extrapolation.
2. R. Fuchs, J.L. Bear, and R.F. Rodewald, *J. Am. Chem. Soc.*, **91**, 5797 (1969); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.



**Solvent, S = N,N-Dimethyl formamide**  $\Delta H_f^\circ(X, W+S)$  / kJ/mol, mol/dm<sup>3</sup> scale, 298.15 K

ref.	1	2	3	4	5	6	7	8	ref.	9	10	11	12	13	14	15	selec-
wt.	1.0	0.2	1.0	0.1	0.5	1.0	1.0	0.1	wt.	0.5	0.2	0.1	0.1	1.0	0.5	1.0	ted
H <sup>+</sup>								-28.0	H <sup>+</sup>								
Li <sup>+</sup>	6.3	-26.4	-32.2		-32.2	-32.2	-32.2		Li <sup>+</sup>	-30	-33.5		-33.2	-33.2			-29.3
Na <sup>+</sup>	-24.7	-39.7	-33.0		-33.0	-33.1	-33.1		Na <sup>+</sup>	-31	-30.1		-33.1	-33.1	-33		-37.4
K <sup>+</sup>	-31.4	-46.4	-39.5		-39.5	-39.3	-39.3		K <sup>+</sup>	-38	-30.1		-39.3	-39.3			-24.8
Rb <sup>+</sup>	-30.1		-37.8		-37.8	-37.7	-37.7		Rb <sup>+</sup>	-37	-33.9		-37.7	-37.7			-36.6
Cs <sup>+</sup>	-28.5		-35.6		-35.5	-36.8	-36.8		Cs <sup>+</sup>	-34	-32.2		-36.8	-36.8			-35.8
Ag <sup>+</sup>				+46.4		-38.5	-38.5		Ag <sup>+</sup>				-85.5	-38.5			-27.8
Me <sub>4</sub> N <sup>+</sup>	-2.5	-17.7	-17.3		-17.3	-16.3			Ba <sup>++</sup>				-62.7	-62.7			-35
Et <sub>4</sub> N <sup>+</sup>		-1.0							Zn <sup>++</sup>				-63.3	-63.3			
Pr <sub>4</sub> N <sup>+</sup>		9.3							Cd <sup>++</sup>								
Bu <sub>4</sub> N <sup>+</sup>		15.0							Me <sub>4</sub> N <sup>+</sup>								-14.0
Ph <sub>4</sub> As <sup>+</sup>	-9.0	-23.0	-19.6		-19.6	-19.7	-19.7		Et <sub>4</sub> N <sup>+</sup>								2.7
Cl <sup>-</sup>	11.7	25.5	12.0		21.1	21.3	21.3	21.3	Pr <sub>4</sub> N <sup>+</sup>								12.8
Br <sup>-</sup>	-5.6	9.6	4.1	8.8	4.1	3.3	3.3		Bu <sub>4</sub> N <sup>+</sup>								19.9
I <sup>-</sup>	-22.6	-5.4	-12.3		-12.3	-13.8	-13.8		Ph <sub>4</sub> As <sup>+</sup>				-19.7	-19.7			-15.7
SCN <sup>-</sup>							-10.0		F <sup>-</sup>	59							
N <sub>3</sub> <sup>-</sup>							-1.0		Cl <sup>-</sup>	21	12.6				21		17.4
ClO <sub>4</sub> <sup>-</sup>	-33.1	-15.5	-22.6	3	-22.6	-25.1	-22.6		Br <sup>-</sup>	1	-2.5						-7.3
CF <sub>3</sub> CO <sub>2</sub> <sup>-</sup>		25.9							I <sup>-</sup>	-16	-10.0						-16.1
CF <sub>3</sub> SO <sub>3</sub> <sup>-</sup>									SCN <sup>-</sup>								
BPh <sub>4</sub> <sup>-</sup>	-9.0	-23.0	-19.6		-19.6	-19.7	-19.7		N <sub>3</sub> <sup>-</sup>		9.2		2.5		-23		-23
									ClO <sub>4</sub> <sup>-</sup>								
									CF <sub>3</sub> CO <sub>2</sub> <sup>-</sup>								
									CF <sub>3</sub> SO <sub>3</sub> <sup>-</sup>								
									BPh <sub>4</sub> <sup>-</sup>								

$\Delta H_f^\circ$  N,N-Dimethyl Formamide - References and Comments

- H. Choux and R.L. Benoit, *J. Am. Chem. Soc.*, **91**, 6221 (1969); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
- R. Fuchs, J.L. Bear, and R.F. Rodewald, *J. Am. Chem. Soc.*, **91**, 5797 (1969); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
- C.V. Krishnan and H.L. Friedman, *J. Phys. Chem.*, **79**, 3606 (1971); using transfer data from W to PC from idem., **73**, 3934 (1969) and the Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
- B.G. Cox and A.J. Parker, *J. Am. Chem. Soc.*, **95**, 402 (1973); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
- M.H. Abraham, *J. Chem. Soc., Faraday Trans. 1*, **69**, 1375 (1973); from correspondence plot, adjusted by addition of +(-) 17.3 kJ/mol to cation (anion) values.
- B.G. Cox, *Ann. Rev. Chem. Soc.*, **70**, 249 (1973); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
- B.G. Cox, G.R. Hedwig, A.J. Parker, and D.W. Watts, *Austr. J. Chem.*, **27**, 477 (1974); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
- R. Domain, M. Rinfret, and R.L. Benoit, *Can. J. Chem.*, **54**, 2101 (1976); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
- G. Somsen and L. Weeda, *J. Electroanal. Chem. Interfac. Electrochem.*, **29**, 375 (1971); electrostatic extrapolation.
- D.S. Gill, J.P. Singla, R.C. Paul, and S.P. Narula, *J. Chem. Soc., Dalton Trans.*, **1972**, 522; extrapolation method.
- B.G. Cox and A.J. Parker, *J. Am. Chem. Soc.*, **95**, 408 (1973); for N<sub>3</sub><sup>-</sup> Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
- G.R. Hedwig and A.J. Parker, *J. Am. Chem. Soc.*, **96**, 6589 (1974); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
- G.R. Hedwig, D.A. Owensby, and A.J. Parker, *J. Am. Chem. Soc.*, **97**, 3888 (1975); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
- A.J. Parker, *Electrochim. Acta*, **21**, 671 (1976); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
- B.G. Cox and W.E. Waghorne, *Chem. Soc. Rev.*, **9**, 381 (1980); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.

**Solvent, S = N,N-Dimethyl formamide (contd.)**  $\Delta S_f^\circ(X, W+S) / J/K \cdot \text{mol}$ , mol/dm<sup>3</sup> scale, 298.15 K

ref.	1	2	3	4	5	6	7	8	9	10	11	Selected
wt.	0.5	1.0	0.5	1.0	0.5	1.0	0.5	0.5	0.1	1.0	1.0	
Li <sup>+</sup>	-69					-75				-76		[-60]
Na <sup>+</sup>	-77			-34	-78	-75	-76	-97		-76		[-81]
K <sup>+</sup>	-98	-96		-76	-86	-100		-110		-100		[-100]
Rb <sup>+</sup>	-94	-94		-93	-92	-93		-105		-93		[-96]
Cs <sup>+</sup>	-88	-87	-94	-93	-94	-93		-99		-93		[-92]
Ag <sup>+</sup>				-72		-72				-72		[-77]
Zn <sup>++</sup>							-111			-215		
Me <sub>4</sub> N <sup>+</sup>	-31				-40			-34		-111		
Et <sub>4</sub> N <sup>+</sup>	31									-100		
Pr <sub>4</sub> N <sup>+</sup>												
Bu <sub>4</sub> N <sup>+</sup>	153						146					
Ph <sub>4</sub> As <sup>+</sup>	82			62	62	62						[-33]
Cl <sup>-</sup>	-90	-72		-83	-85	-83	-84	-95				[31]
Br <sup>-</sup>	-91	-87	-88	-90	-103	-90		-103				[151]
I <sup>-</sup>	-102	-87		-110	-102	-110		-107				[68]
SCN <sup>-</sup>						-88						[-85]
N <sub>3</sub> <sup>-</sup>				-111		-111	-79	-108				[-92]
ClO <sub>4</sub> <sup>-</sup>	-77			62	-91	-77			-83			[-105]
BPh <sub>4</sub> <sup>-</sup>	82			62	62	62						[-111]
												[-125]
												[-86]
												[68]

$\Delta S_f^\circ$  Dimethylformamide - References and Comments

1. C.M. Criss, R.P. Held, and E. Luksha, *J. Phys. Chem.*, **72**, 2970 (1968); correspondence method (linear dependence on aqueous entropies).
2. M.H. Abraham, *J. Chem. Soc. Chem. Commun.*, **1972**, 888; from correspondence plot.
3. B.G. Cox and A.J. Parker, *J. Am. Chem. Soc.*, **95**, 402 (1973); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
4. M.H. Abraham, *J. Chem. Soc.*, *Faraday Trans. 1*, **69**, 1375 (1973); from correspondence plot.
5. B.G. Cox, *Ann. Rev. Chem. Soc.*, **70**, 249 (1973); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
6. B.G. Cox, G.R. Hedwig, A.J. Parker, and D.W. Watts, *Austr. J. Chem.*, **27**, 477 (1974); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
7. A.J. Parker, *Electrochim. Acta*, **21**, 671 (1976); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
8. M.H. Abraham and J. Liszi, *J. Chem. Soc., Faraday Trans. 1*, **74**, 2858 (1978); electrostatic calculation.
9. B.G. Cox and A.J. Parker, *J. Am. Chem. Soc.*, **95**, 408 (1973); for N<sub>3</sub><sup>-</sup> Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
10. G.R. Hedwig, D.A. Owensby, and A.J. Parker, *J. Am. Chem. Soc.*, **97**, 3888 (1975); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
11. B.G. Cox and W.E. Waghorne, *Chem. Soc. Rev.*, **9**, 381 (1980); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.

**Solvent, S = Dimethyl acetamide** | **Solvent, S = N,N,N',N'-Tetramethyl urea**

$\Delta H_t^\circ(X, W+S) / \text{kJ/mol, mol/dm}^3$ scale, 298.15 K		$\Delta H_t^\circ(X, W+S) / \text{kJ/mol, mol/dm}^3$ scale, 298.15 K	
ref.	1	ref.	2
wt.	0	wt.	0
Li <sup>+</sup>	17.6	Li <sup>+</sup>	12.4
Na <sup>+</sup>	-1.3	Na <sup>+</sup>	1.7
K <sup>+</sup>	5.0	K <sup>+</sup>	15.7
Rb <sup>+</sup>	-0.4	Rb <sup>+</sup>	11.9
Cs <sup>+</sup>	-3.3	Cs <sup>+</sup>	6.9
Cl <sup>-</sup>	-23.8	NH <sub>4</sub> <sup>+</sup>	2.3
		Me <sub>4</sub> N <sup>+</sup>	66.6
		Br <sup>-</sup>	-39.3
		SCN <sup>-</sup>	-17.2
		ClO <sub>4</sub> <sup>-</sup>	-41.2

References and Comments

1. R.C. Paul, J.S. Banait, and S.P. Narula, *J. Electroanal. Chem. Interfac. Electrochem.*, **66**, 111 (1975); extrapolation method.
2. R.C. Paul, S.P. Jankar, J.S. Banait, and S.P. Narula, *J. Chem. Soc. Faraday Trans. 1*, **73**, 833 (1977); extrapolation method.

**Solvent, S = N-Methyl pyrrolidinone**

$\Delta H_t^\circ(X, W+S) / \text{kJ/mol, mol/dm}^3$ scale, 298.15 K					$\Delta S_t^\circ(X, W+S) / \text{J/K}\cdot\text{mol, mol/dm}^3$ scale, 298 K	
ref.	1	2	3	selec-	ref.	2
wt.	1.0	1.0	0.5	ted	wt.	1.0
Li <sup>+</sup>	-26.4				Na <sup>+</sup>	-77
Na <sup>+</sup>	-43.5	-39.3		-41	Cl <sup>-</sup>	-104
K <sup>+</sup>	-49.8	-43.9		-47	Br <sup>-</sup>	-104
Bu <sub>4</sub> N <sup>+</sup>			9.9		I <sup>-</sup>	-87
Ph <sub>4</sub> As <sup>+</sup>	-15.9	-17.6		-17		
Cl <sup>-</sup>	28.9	24.3		27		
Br <sup>-</sup>	14.2	9.6	15.6	13		
I <sup>-</sup>	5.4	-1.7		2		
ClO <sub>4</sub> <sup>-</sup>	-6.7		-19.7	-11		
BBu <sub>4</sub> <sup>+</sup>			9.9			
BPh <sub>4</sub> <sup>-</sup>	-15.9	-17.6		-17		

N-Methyl Pyrrolidinone -References and Comments

1. R. Fuchs, J.L. Bear, and R.F. Rodewald, *J. Am. Chem. Soc.*, **91**, 5797 (1969); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
2. B.G. Cox, G.R. Hedwig, A.J. Parker, and D.W. Watts, *Austr. J. Chem.*, **27**, 477 (1974); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
3. Y. Kondo, K. Yuki, T. Yoshida, and N. Tokura, *J. Chem. Soc., Faraday Trans. 1*, **76**, 812 (1980); Bu<sub>4</sub>NBBu<sub>4</sub> assumption.

**Solvent, S = Nitromethane**

$\Delta H_t^\circ(X, W+S) / \text{kJ/mol, mol/dm}^3$ scale, 298.15 K		$\Delta S_t^\circ(X, W+S) / \text{J/K}\cdot\text{mol, mol/dm}^3$ scale, 298.15 K	
ref.	1	ref.	1
wt.	0	wt.	0
N <sub>3</sub> <sup>-</sup>	4.2	N <sub>3</sub> <sup>-</sup>	-76

 $\Delta H_t^\circ$  and  $\Delta S_t^\circ$  Nitromethane - References and Comments

1. B.G. Cox and A.J. Parker, *J. Am. Chem. Soc.*, **95**, 408 (1973); for N<sub>3</sub><sup>-</sup> Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.

**Solvent, S = Acetonitrile** $\Delta H_t^\circ$  (X, W→S) / kJ/mol, mol/dm<sup>3</sup> scale, 298.15 K

ref.	1	2	3	4	5	6	7	8
wt.	0.5	1.0	0.2	0	1.0	0.5	0.2	1.0
H <sup>+</sup>							56.1	
Li <sup>+</sup>								
Na <sup>+</sup>	-14.4	-13.0			-13.0			-12.3
K <sup>+</sup>	-23.0	-22.6			-22.6	-23		
Rb <sup>+</sup>	-23.2	-25.9			-23.0			
Cs <sup>+</sup>								
Ag <sup>+</sup>		-52.7			-52.7	-53		-52.1
Ba <sup>++</sup>				-8.5				
Mn <sup>++</sup>								
Ni <sup>++</sup>								
Zn <sup>++</sup>				20.1		20		
Cd <sup>++</sup>				8.2				
Me <sub>4</sub> N <sup>+</sup>	-15.3	-15.5						
Et <sub>4</sub> N <sup>+</sup>								
Pr <sub>4</sub> N <sup>+</sup>								
Bu <sub>4</sub> N <sup>+</sup>								
Ph <sub>4</sub> P <sup>+</sup>								
Ph <sub>4</sub> As <sup>+</sup>	-17.6	-10.5		-11.7	-10.5			-11.1
Cl <sup>-</sup>	17.4	19.7					23.4	19.0
Br <sup>-</sup>	7.9	8.4			8.4			
I <sup>-</sup>	-7.1	-7.1			-7.1			-9.0
N <sub>3</sub> <sup>-</sup>		8.8	8.4		8.8			
ClO <sub>4</sub> <sup>-</sup>	-17.0							
CF <sub>3</sub> SO <sub>3</sub> <sup>-</sup>				2.5				
BPh <sub>4</sub> <sup>-</sup>		-10.5		-11.7	-10.5			-11.1

  

ref.	9	10	11	12	13	14	15	selected
wt.	1.0	0.5	1.0	1.0	1.0	0.5	0.5	
Li <sup>+</sup>			1.1				-0.3	
Na <sup>+</sup>	-13.6		-13.6	-12.5	-13.2		-14.1	-13.3
K <sup>+</sup>	-22.6		-23.2				-23.1	-22.9
Rb <sup>+</sup>	-23.0		-25.7					-24.6
Cs <sup>+</sup>			-26.1				-25.6	
Ag <sup>+</sup>	-52.7		-53.3		-41.2			-52.7
Ba <sup>++</sup>	-8.5	-8.6						
Mn <sup>++</sup>		21.6				16.8		
Fe <sup>++</sup>						8.7		
Co <sup>++</sup>						-0.3		
Ni <sup>++</sup>		-46.0				-4.8		
Cu <sup>++</sup>						11.5		
Zn <sup>++</sup>	20.1					21.5		
Cd <sup>++</sup>	8.2							
Me <sub>4</sub> N <sup>+</sup>			-15.7	-13.7			-14.7	-15.3
Et <sub>4</sub> N <sup>+</sup>			-1.4	-3.1	-1.8			-2.1
Pr <sub>4</sub> N <sup>+</sup>			9.9	8.9				
Bu <sub>4</sub> N <sup>+</sup>			18.2	17.1	19.2			18.1
Ph <sub>4</sub> P <sup>+</sup>				-9.2				
Ph <sub>4</sub> As <sup>+</sup>			-9.8		-10.2			-11.1
Cl <sup>-</sup>					20.5			19.3
Br <sup>-</sup>			7.7	6.9	7.9		9.2	8.0
I <sup>-</sup>			-7.4		-7.0		(-7.6)	-7.6
N <sub>3</sub> <sup>-</sup>								8.8
ClO <sub>4</sub> <sup>-</sup>			-17.8		-16.2		-17.2	-17.0 <sup>2</sup>
BPh <sub>4</sub> <sup>-</sup>			-9.8	-9.2	-10.2			-10.4

 $\Delta H_t^\circ$  Acetonitrile - References and Comments

1. M.H. Abraham, *J. Chem. Soc., Faraday Trans. 1*, **69**, 1375 (1973); from correspondence plot.
2. B.G. Cox, *Ann. Rev. Chem. Soc.*, **70**, 249 (1973); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
3. B.G. Cox and A.J. Parker, *J. Am. Chem. Soc.*, **95**, 408 (1973); for N<sub>3</sub><sup>-</sup> Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
4. G.R. Hedwig and A.J. Parker, *J. Am. Chem. Soc.*, **96**, 6589 (1974); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.

5. B.G. Cox, G.R. Hedwig, A.J. Parker, and D.W. Watts, *Austr. J. Chem.*, **27**, 477 (1974);  $\text{Ph}_4\text{AsBPh}_4$  assumption.
6. A.J. Parker, *Electrochim. Acta*, **21**, 671 (1976);  $\text{Ph}_4\text{AsBPh}_4$  assumption.
7. R. Domain, M. Rinfret, and R.L. Benoit, *Can. J. Chem.*, **54**, 2101 (1976);  $\text{Ph}_4\text{AsBPh}_4$  assumption.
8. B.G. Cox, R. Natarajan, and W.E. Waghorne, *J. Chem. Soc. Faraday Trans. 1*, **75**, 86 (1979);  $\text{Ph}_4\text{AsBPh}_4$  assumption.
9. G.R. Hedwig, D.A. Owensby, and A.J. Parker, *J. Am. Chem. Soc.*, **97**, 3888 (1975);  $\text{Ph}_4\text{AsBPh}_4$  assumption.
10. J.F. Coetzee and E.J. Subak, Jr., *Rev. Chim. Miner.*, **15**, 40 (1979); using data for transfer of  $\text{ClO}_4^-$  from W to MeCN from ref. 5.
11. B.G. Cox and W.E. Waghorne, *Chem. Soc. Rev.*, **9**, 381 (1980);  $\text{Ph}_4\text{AsBPh}_4$  assumption.
12. A. Mayaffre and R. Bury, *Jour. Calorim. Therm.*, **11**, 3.22-1 (1980);  $\text{Ph}_4\text{PBPh}_4$  assumption.
13. S. Ahrland, S. Ishiguro, and R. Portanova, priv. commun. (correction) and to be published; quoted in S. Ahrland, *Pure Appl. Chem.*, **54**, 14 (1982);  $\text{Ph}_4\text{AsBPh}_4$  assumption.
14. W. Libus, M. Mecik, and H. Strzelecki, *J. Soln. Chem.*, **9**, 723 (1980) using  $\Delta H_t^\circ(\text{ClO}_4^-, \text{W} \rightarrow \text{MeCN})$  from ref. 3.
15. Y.-S. Choi and C.M. Criss, *J. Chem. Eng. Data*, **22**, 297 (1977); using heats of solution in water from V.B. Parker, *NSRDS-NBS-2* (1964) and  $\Delta H_t^\circ(\text{H}_2\text{O} \rightarrow \text{MeCN})$  from ref. 5.

### Solvent, S = Acetonitrile (contd.)

$\Delta S_t^\circ(X, \text{W} \rightarrow \text{S}) / \text{J/K}\cdot\text{mol}$ , mol/dm<sup>3</sup> scale, 298.15 K

ref.	1	2	3	4	5	6	7	8	9	selected
wt.	0.5	0.5	1.0	0.2	1.0	1.0	0.5	0.2	1.0	
$\text{Li}^+$										-73
$\text{Na}^+$		-96	-87		-90	-90		-85	-91	-90
$\text{K}^+$	-102	-102	-102		-102	-103	-111	-80	-103	-103
$\text{Rb}^+$	-97	-95	-110		-100	-100		-93	-109	-103
$\text{Cs}^+$								-88	-102	-100
$\text{Ag}^+$			-104		-104	-104	-104		-102	-100
$\text{Ba}^{++}$						-221				
$\text{Zn}^{++}$						-163	-164			
$\text{Cd}^{++}$						-114				
$\text{Me}_4\text{N}^+$	-43	-43						-22	-43	[-41]
$\text{Et}_4\text{N}^+$	26								46	39
$\text{Pr}_4\text{N}^+$	100									
$\text{Bu}_4\text{N}^+$	154									
$\text{Ph}_4\text{As}^+$		66	74		74				77	74
$\text{Cl}^-$		-75	-76					-83	-70	-74
$\text{Br}^-$		-78	-65		-79			-91	-79	-76
$\text{I}^-$	-68	-86	-87		-88			-95	-89	-85
$\text{N}_3^-$			-69	-77	-73					[-72]
$\text{ClO}_4^-$	-59	-75						-97	-72	-72
$\text{BPh}_4^-$			74		74				77	75

### $\Delta S_t^\circ$ Acetonitrile - References and Comments

1. M.H. Abraham, *J. Chem. Soc. Chem. Comm.*, **1972**, 888; assumption that  $\Delta S_t^\circ(\text{Me}_4\text{N}^+, \text{W} \rightarrow \text{S}) = 0$ .
2. M.H. Abraham, *J. Chem. Soc.*, *Faraday Trans. 1*, **69**, 1375 (1973); from correspondence plot.
3. B.G. Cox, *Ann. Rev. Chem. Soc.*, **70**, 249 (1973);  $\text{Ph}_4\text{AsBPh}_4$  assumption.
4. B.G. Cox and A.J. Parker, *J. Am. Chem. Soc.*, **95**, 408 (1973); for  $\text{N}_3^-$   $\text{Ph}_4\text{AsBPh}_4$  assumption.
5. B.G. Cox, G.R. Hedwig, A.J. Parker, and D.W. Watts, *Aust. J. Chem.*, **27**, 477 (1974);  $\text{Ph}_4\text{AsBPh}_4$  assumption.
6. G.R. Hedwig, D.A. Owensby, and A.J. Parker, *J. Am. Chem. Soc.*, **97**, 3888 (1975);  $\text{Ph}_4\text{AsBPh}_4$  assumption.
7. A.J. Parker, *Electrochim. Acta*, **21**, 671 (1976);  $\text{Ph}_4\text{AsBPh}_4$  assumption.
8. M.H. Abraham and J. Liszi, *J. Chem. Soc.*, *Faraday Trans. 1*, **74**, 2858 (1978); electrostatic calculation.
9. B.G. Cox and W.E. Waghorne, *Chem. Soc. Rev.*, **9**, 381 (1980);  $\text{Ph}_4\text{AsBPh}_4$  assumption.

**Solvent, S = Dimethyl sulfoxide** $\Delta H_{\ddagger}^{\circ}(X, W+S) / \text{kJ/mol, mol/dm}^3 \text{ scale, 298.15 K}$ 

ref.	1	2	3	4	5	6	7	8	9	10	11	12
wt.	1.0	1.0	0.5	1.0	0.2	0.5	0.1	0.1	1.0	0.5	1.0	0.5
H <sup>+</sup>						-25.5		-25.5				
Li <sup>+</sup>		-27.2	32.5	-28.9			-31			-26.4	-26.4	
Na <sup>+</sup>	-29.9	-30.1	7.5	-30.5			-20		-30.1	-27.7	-27.6	
K <sup>+</sup>	-37.0	-35.4	-8.9	-36.8			-23	-33.5		-34.9	-34.7	
Rb <sup>+</sup>			-15.6							-33.5	-33.4	
Cs <sup>+</sup>	-32.6	-34.5	-21.3							-32.4	-32.2	
Ag <sup>+</sup>					-54.0						-54.8	
Ba <sup>++</sup>												
Zn <sup>++</sup>												
Cd <sup>++</sup>												
Hg <sup>++</sup>												
NH <sub>4</sub> <sup>+</sup>								-39.8				
Me <sub>4</sub> N <sup>+</sup>			-17.3							-15.3	-16.3	
Et <sub>4</sub> N <sup>+</sup>												
Pr <sub>4</sub> N <sup>+</sup>												
Bu <sub>4</sub> N <sup>+</sup>												
Ph <sub>4</sub> As <sup>+</sup>	-9.7	-9.6	-17.3	-8.8						(-10.9	-11.9	-11.7)
Cl <sup>-</sup>	20.5	21.3	24.8	20.1		18.8	18		19.7	18.8	18.8	
Br <sup>-</sup>	5.6	4.6	23.7	5.9	5.0				4.2	3.5	3.3	
I <sup>-</sup>	-10.5	-10.9	6.2	-9.2					-10.5	-12.8	-13.4	
N <sub>3</sub> <sup>-</sup>											-2.5	-3.3
OH <sup>-</sup>												
ClO <sub>4</sub> <sup>-</sup>		-20.1	-13.6	-15.9						-19.1	-19.2	
CF <sub>3</sub> SO <sub>3</sub> <sup>-</sup>												
BPh <sub>4</sub> <sup>-</sup>	-9.7	-9.6	-17.3	-8.8					-10.9	-11.9	-11.7	

 $\Delta H_{\ddagger}^{\circ}$  Dimethyl Sulfoxide - References and Comments

1. E.M. Arnett and D.R. McKelvey, *J. Am. Chem. Soc.*, **88**, 2598 (1966); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
2. H. Choux and R.L. Benoit, *J. Am. Chem. Soc.*, **91**, 6221 (1969); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
3. C.V. Krishnan and H.L. Friedman, *J. Phys. Chem.*, **73**, 3934 (1969); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
4. R. Fuchs, J.L. Bear, and R.F. Rodewald, *J. Am. Chem. Soc.*, **91**, 5797 (1969); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
5. B.G. Cox and A.J. Parker, *J. Am. Chem. Soc.*, **95**, 402 (1973); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
6. R. Domain, M. Rinfret, and R.L. Benoit, *Can. J. Chem.*, **54**, 2101 (1976); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
7. A.K.R. Unni, N. Sitaraman, and V.K.C. Menon, *J. Indian Chem. Soc.*, **54**, 1021 (1977); electrostatic calculation or extrapolation.
8. E. Milanova, S.Y. Lam, B. Desjardins, and R.L. Benoit, *Adv. Chem. Ser.*, **177**, 145 (1979); the extrathermodynamic assumption is not stated.
9. R. Fuchs and C.P. Hagan, *J. Phys. Chem.*, **77**, 1797 (1973); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
10. M.H. Abraham, *J. Chem. Soc., Faraday Trans. 1*, **69**, 1375 (1973); from correspondence plot.
11. B.G. Cox, *Ann. Rev. Chem. Soc.*, **70**, 249 (1973); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
12. B.G. Cox and A.J. Parker, *J. Am. Chem. Soc.*, **95**, 408 (1973); for N<sub>3</sub><sup>-</sup> Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
13. B.G. Cox, G.R. Hedwig, A.J. Parker, and D.W. Watts, *Austr. J. Chem.*, **27**, 477 (1974); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
14. G.R. Hedwig and A.J. Parker, *J. Am. Chem. Soc.*, **96**, 6589 (1974); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
15. R. Fuchs, C.P. Hagan, and R.F. Rodewald, *J. Phys. Chem.*, **78**, 1509 (1974); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
16. S. Ahrlund, L. Kullberg, and R. Portanova, *Acta Chem. Scand.*, **32A**, 251 (1978); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
17. E.M. Arnett and T.C. Moriarty, *J. Am. Chem. Soc.*, **93**, 4908 (1971); using  $\Delta H_{\ddagger}^{\circ}(I^{-}, W+DMSO) = -11.4 \text{ kJ/mol}$ , as the average of the compiled values, and  $\Delta H_{\ddagger}^{\circ}(Br^{-}, W+DMSO)$  from ref. 18.
18. G.R. Hedwig, D.A. Owensby, and A.J. Parker, *J. Am. Chem. Soc.*, **97**, 3888 (1975); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
19. E.M. Arnett and L.E. Small, *J. Am. Chem. Soc.*, **99**, 808 (1977); using  $\Delta H_{\ddagger}^{\circ}(I^{-}, W+DMSO) = -11.4 \text{ kJ/mol}$ , as the average of the compiled values.
20. J.F. Coetzee and E.J. Subak, Jr., *Rev. Chim. Miner.*, **15**, 40 (1979); using  $\Delta H_{\ddagger}^{\circ}(ClO_4^{-}, W+DMSO)$  from ref. 13.
21. B.G. Cox and W.E. Waghorne, *Chem. Soc. Rev.*, **9**, 381 (1980); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
22. W. Libus, M. Mecik, and H. Strzelecki, *J. Soln. Chem.*, **9**, 723 (1980); using  $\Delta H_{\ddagger}^{\circ}(ClO_4^{-}, W+DMSO)$  from ref. 13.

**Solvent, S = Dimethyl sulfoxide (contd.)** $\Delta H_{\text{t}}^{\circ}(X, W+S) / \text{kJ/mol, mol/dm}^3 \text{ scale, 298.15 K}$ 

ref.*	13	14	15	16	17	18	19	20	21	22	selected
wt.	1.0	0.8	1.0	0	0.5	1.0	0.1	1.0	1.0	0.5	
H <sup>+</sup>											
Li <sup>+</sup>	-26.4				-49	-26.4			-26.5		-27.1
Na <sup>+</sup>	-27.6		-30.5		-30.3	-27.6			-28.5		-29.2
K <sup>+</sup>	-34.7				-36.6	-34.7			-35.2		-35.4
Rb <sup>+</sup>	-33.5					-33.5			-38.2		-35
Cs <sup>+</sup>	-32.2				-33.8	-32.2			-33.4		-33.0
Ag <sup>+</sup>	-54.8					-54.8			-50.1		-53.3
Ba <sup>++</sup>		-78.5				-78.5					-80
Mn <sup>++</sup>								-82.4			
Fe <sup>++</sup>								-62.8			
Co <sup>++</sup>										-71.1	
Ni <sup>++</sup>										-72.0	
Cu <sup>++</sup>										-68.3	
Zn <sup>++</sup>		-62.2		-60		-62.2				-63.1	
Cd <sup>++</sup>		-70.8		-67		-70.8				-67.1	
Hg <sup>++</sup>				-76						-64.3	-62
NH <sub>4</sub> <sup>+</sup>											
Me <sub>4</sub> N <sup>+</sup>									-41.0		-41
Et <sub>4</sub> N <sup>+</sup>									-16.6		-16.4
Pr <sub>4</sub> N <sup>+</sup>									3.9		
Bu <sub>4</sub> N <sup>+</sup>									16.0		
Ph <sub>4</sub> As <sup>+</sup>	-11.7	-10.5	-10.9						25.6		
F <sup>-</sup>					30				-11.2		-10.6
Cl <sup>-</sup>	18.8						43		17.1		20.0
Br <sup>-</sup>	3.3		4.2				26		3.6		4.6
I <sup>-</sup>	-13.4				(-11.4)		(-11.4)		-12.0		-11.5
N <sub>3</sub> <sup>-</sup>	-2.5										
OH <sup>-</sup>			74.1								
NO <sub>3</sub> <sup>-</sup>									4.8		
ClO <sub>4</sub> <sup>-</sup>	-19.2								-18.4		-18.2
CF <sub>3</sub> SO <sub>3</sub> <sup>-</sup>		1.2									
BPh <sub>4</sub> <sup>-</sup>	-11.7	-10.5	-10.9						-11.2		-11.0

\*References on the facing page

**Solvent, S = Dimethyl sulfoxide (contd.)** $\Delta S_{\text{t}}^{\circ}(X, W+S) / \text{J/K}\cdot\text{mol, mol/dm}^3 \text{ scale, 298.15 K}$ 

ref.	1	2	3	4	5	6	7	8	selected
wt.	0.2	1.0	0.2	0.5	1.0	1.0	0.2	1.0	
Li <sup>+</sup>		-39		-30	-39	-39		-58	-43
Na <sup>+</sup>		-44		-45	-46	-46	-83	-77	-56
K <sup>+</sup>		-76		-76	-76	-76	-96	-100	-84
Rb <sup>+</sup>		-76		-76	-76	-76	-91	-114	-87
Cs <sup>+</sup>		-66		-68	-66	-66	-85	-91	-74
Ag <sup>+</sup>	-65	-72			-72	-72		-128	[-89]
Ba <sup>++</sup>						-179			
Zn <sup>++</sup>						-56			
Cd <sup>++</sup>						-44			
Me <sub>4</sub> N <sup>+</sup>				-34			-21	-20	[-24]
Et <sub>4</sub> N <sup>+</sup>								39	
Ph <sub>4</sub> As <sup>+</sup>		84		84	84			87	85
Cl <sup>-</sup>		-66		-66	-66		-81	-47	-62
Br <sup>-</sup>	-72	-74		-79	-74		-90	-51	-81
I <sup>-</sup>		-90		-99	-76		-94	-95	-86
N <sub>3</sub> <sup>-</sup>		-88	-97		-94				-92
ClO <sub>4</sub> <sup>-</sup>				-75	-60		-95		-69
BPh <sub>4</sub> <sup>-</sup>		84		84	84			87	85

 $\Delta S_{\text{t}}^{\circ}$  Dimethylsulfoxide - References and Comments

- B.G. Cox and A.J. Parker, *J. Am. Chem. Soc.*, **95**, 402 (1973); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
- B.G. Cox, *Ann. Rev. Chem. Soc.*, **70**, 249 (1973); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
- B.G. Cox and A.J. Parker, *J. Am. Chem. Soc.*, **95**, 408 (1973); for N<sub>3</sub><sup>-</sup> Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
- M.H. Abraham, *J. Chem. Soc., Faraday Trans. 1*, **69**, 1375 (1973); from correspondence plot; adjusted by adding +(-) 26 J/K·mol to cation (anion) values.
- B.G. Cox, G.R. Hedwig, A.J. Parker, and D.W. Watts, *Austr. J. Chem.*, **27**, 477 (1974); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
- G.R. Hedwig, D.A. Owensby, and A.J. Parker, *J. Am. Chem. Soc.*, **97**, 3888 (1975); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
- M.H. Abraham and J. Liszi, *J. Chem. Soc., Faraday Trans. 1*, **74**, 2858 (1978); electrostatic calculation.
- B.G. Cox and W.E. Waghorne, *Chem. Soc. Rev.*, **9**, 381 (1980); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.

**Solvent, S = Tetrahydrothiophene S,S-dioxide (Sulfolane)** $\Delta H_t^\circ(X, W \rightarrow S)$  / kJ/mol, mol/dm<sup>3</sup> scale, 303.15 K

ref.	1	2	3	4	5	6	7,8	9	select-
wt.	1.0	0.5	0.5	1.0	0.5	0.5	0	0.5	ted
H <sup>+</sup>		72.8				72.8			73
Li <sup>+</sup>	22.6							12.5	
Na <sup>+</sup>	-16.9			-15.1				-18.3	-16
K <sup>+</sup>	-26.8			-25.1		-25.1		-29.1	-26
Rb <sup>+</sup>	-28.5			-26.8					-28
Cs <sup>+</sup>	-26.4			-24.7				-29.0	-26
Ag <sup>+</sup>		-16.3		-13.4					-14
Ni <sup>++</sup>							75.7 <sup>8)</sup>		
Me <sub>4</sub> N <sup>+</sup>								-20.3	
Ph <sub>4</sub> N <sup>+</sup>							-9.2 <sup>7)</sup>		
Ph <sub>4</sub> As <sup>+</sup>	-11.9			-10.5					-11
Cl <sup>-</sup>	28.0			25.9	25.9				27
Br <sup>-</sup>	14.0	14.2		12.1				8.8	13
I <sup>-</sup>	-6.7			-8.8				(-7.7)	-8
N <sub>3</sub> <sup>-</sup>			15.1	15.5					15
ClO <sub>4</sub> <sup>-</sup>	-19.7							-13.2	
BPh <sub>4</sub> <sup>-</sup>	-11.9			-10.5					-11

 $\Delta S_t^\circ(X, W \rightarrow S)$  / J/K·mol, mol/dm<sup>3</sup> scale, 303.15 K

ref.	2	3	4	ref.	2	3	4
wt.	0.5	0	1.0	wt.	0.5	0	1.0
Na <sup>+</sup>			-41	Cl <sup>-</sup>			-90
K <sup>+</sup>			-70	Br <sup>-</sup>	-90		-93
Rb <sup>+</sup>			-60	I <sup>-</sup>			-98
Cs <sup>+</sup>			-49	N <sub>3</sub> <sup>-</sup>		-86	-81
Ag <sup>+</sup>	-38		-32	BPh <sub>4</sub> <sup>-</sup>			84
Ph <sub>4</sub> As <sup>+</sup>			84				

 $\Delta H_t^\circ$  and  $\Delta S_t^\circ$  Tetrahydrothiophene S,S-Dioxide - References and Comments

- H. Choux and R.L. Benoit, *J. Am. Chem. Soc.*, **91**, 6221 (1969); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
- B.G. Cox and A.J. Parker, *J. Am. Chem. Soc.*, **95**, 402 (1973); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
- B.G. Cox and A.J. Parker, *J. Am. Chem. Soc.*, **95**, 408 (1973); for N<sub>3</sub><sup>-</sup> Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
- B.G. Cox, G.R. Hedwig, A.J. Parker, and D.W. Watts, *Austr. J. Chem.*, **27**, 477 (1974); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
- R. Domain, M. Rinfret, and R.L. Benoit, *Can. J. Chem.*, **54**, 2101 (1976); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
- E. Milanova, S.Y. Lam, B. Desjardins, and R.L. Benoit, *Adv. Chem. Ser.*, **177**, 145 (1979); the extrathermodynamic assumption is not stated.
- M. Castagnolo, G. Petrella, M. Della Monica, and A. Sacco, *J. Soln. Chem.*, **8**, 501 (1979); Ph<sub>4</sub>PBPh<sub>4</sub> assumption.
- J.F. Coetzee and E.J. Subak, Jr., *Rev. Chim. Miner.*, **15**, 40 (1979); using  $\Delta H_t^\circ(\text{ClO}_4^-, W \rightarrow \text{TMS})$  from ref. 4.
- Y.-S. Choi and C.M. Criss, *J. Chem. Eng. Data*, **22**, 297 (1977); using heats of solution in water from V.B. Parker, NSRDS-NBS-2 (1964) (at 298.15 K) and  $\Delta H_t^\circ(\text{I}^-, W \rightarrow \text{TMS})$  from ref. 4.



**Solvent, S = Hexamethyl phosphoric triamide**

$\Delta H_t^\circ(X, W \rightarrow S) / \text{kJ/mol, mol/dm}^3 \text{ scale, } 298.15 \text{ K}$				$\Delta S_t^\circ(X, W \rightarrow S) / \text{J/K}\cdot\text{mol, mol/dm}^3 \text{ scale, } 298.15 \text{ K}$	
ref.	1	2	3	1	2
wt.	0	1.0	0	0	0
Li <sup>+</sup>			-66		
Na <sup>+</sup>			-37		
K <sup>+</sup>		-57.9	-49		-138
Rb <sup>+</sup>			-67		
Cs <sup>+</sup>			-71		
Ag <sup>+</sup>					
Ba <sup>++</sup>		-144.6			
Zn <sup>++</sup>		-97.4			-146
Cd <sup>++</sup>		-116.1			-249
Ph <sub>4</sub> As <sup>+</sup>		-13.7			
Cl <sup>-</sup>					
Br <sup>-</sup>					
N <sub>3</sub> <sup>-</sup>	13.4			-97	
BPh <sub>4</sub> <sup>-</sup>		-13.7			

Hexamethyl Phosphoric Triamide - References and Comments

1. B.G. Cox and A.J. Parker, *J. Am. Chem. Soc.*, *95*, 408 (1973); for N<sub>3</sub><sup>-</sup> Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
2. G.R. Hedwig, D.A. Owensby, and A.J. Parker, *J. Am. Chem. Soc.*, *97*, 3888 (1975); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.
3. G.R. Stevenson, I. Valentin, E. Williams, Jr., G. Caldwell, and A.E. Alegria, *J. Am. Chem. Soc.*, *101*, 515 (1979); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption.

**Solvent, S = 1,1-Dichloroethane**
 $\Delta S_t^\circ(X, W \rightarrow S) / \text{J/K}\cdot\text{mol, mol/dm}^3 \text{ scale, } 298.15 \text{ K}$ 

ref.	1	ref.	1
wt.	0	wt.	0
Na <sup>+</sup>	-152	Cl <sup>-</sup>	-150
K <sup>+</sup>	-165	Br <sup>-</sup>	-158
Rb <sup>+</sup>	-160	I <sup>-</sup>	-162
Cs <sup>+</sup>	-154	ClO <sub>4</sub> <sup>-</sup>	-164
Me <sub>4</sub> N <sup>+</sup>	-89		

 $\Delta S_t^\circ$  1,1-Dichloroethane - References and Comments

1. M.H. Abraham and J. Liszi, *J. Chem. Soc., Faraday Trans. 1*, *74*, 2858 (1978); electrostatic calculation.

**Solvent, S = 1,2-Dichloroethane** $\Delta H_t^\circ(X, W+S)$  / kJ/mol, mol/dm<sup>3</sup> scale, 298.15 K

ref.	1	ref.	1
wt.	1.0	wt.	1.0
Na <sup>+</sup>	-25.1	Cl <sup>-</sup>	16.3
K <sup>+</sup>	-28.0	Br <sup>-</sup>	0.8
Rb <sup>+</sup>	-27.6	I <sup>-</sup>	-15.5
Cs <sup>+</sup>	-27.2	ClO <sub>4</sub> <sup>-</sup>	-24.3
Me <sub>4</sub> N <sup>+</sup>	-15.9	BPh <sub>4</sub> <sup>-</sup>	-22.6
Et <sub>4</sub> N <sup>+</sup>	-10.0		
Bu <sub>4</sub> N <sup>+</sup>	9.0		
Ph <sub>4</sub> As <sup>+</sup>	-22.6		

 $\Delta S_t^\circ(X, W+S)$  / J/K·mol, mol/dm<sup>3</sup> scale, 298.15 K

ref.	1	2	ref.	1	2
wt.	1.0	0	wt.	1.0	0
Li <sup>+</sup>	-155		F <sup>-</sup>	-100	
Na <sup>+</sup>	-167	-147	Cl <sup>-</sup>	-126	-145
K <sup>+</sup>	-180	-160	Br <sup>-</sup>	-130	-153
Rb <sup>+</sup>	-176	-155	I <sup>-</sup>	-138	-157
Cs <sup>+</sup>	-172	-149	ClO <sub>4</sub> <sup>-</sup>	-138	-159
Me <sub>4</sub> N <sup>+</sup>	-105	-84	BPh <sub>4</sub> <sup>-</sup>	34	
Et <sub>4</sub> N <sup>+</sup>	-50				
Bu <sub>4</sub> N <sup>+</sup>	88				
Ph <sub>4</sub> As <sup>+</sup>	34				

1,2-Dichloroethane - References and Comments

1. M.H. Abraham, A.F. Danil de Namor, and R.A. Schulz, *J. Soln. Chem.*, **5**, 529 (1976); Ph<sub>4</sub>AsBPh<sub>4</sub> assumption and correspondence plot.
2. M.H. Abraham and J. Liszi, *J. Chem. Soc., Faraday Trans. 1*, **74**, 2858 (1978); electrostatic calculation.