IONS IN SOLUTION:
Basic Principles of
Chemical Interactions

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Author's preface

The general area of inorganic solution chemistry is treated rather cursorily in many undergraduate textbooks. A number of readers of the author's *Metal Ions in Solution* have over the years suggested that an undergraduate-level version would be a useful teaching aid. The initial response was to plan a pair of cassettes with accompanying workbooks, to be produced by the Educational Techniques Subject Group of the Royal Society of Chemistry. The first of these appeared in 1984, the second is in preparation. Meanwhile it has been decided to make this material available in conventional textbook format. The first draft of the manuscript for this book consisted simply of the scripts for the cassettes. Subsequent versions have involved a little rearrangement and considerable rewriting, but the scope and level of the text remain very similar to those of the cassettes. The solution chemistry of simple anions and of a selection of complexes has been added to that of metal cations, to give a more balanced coverage of inorganic species. Topics dealt with include the extent and nature of solvation, and some spectroscopic, thermodynamic, and kinetic characteristics of inorganic ions in solution. Much of the book is devoted to aqueous solutions, but several sections reflect greater knowledge of certain aspects in non-aqueous media. Some basic knowledge of inorganic and physical chemistry is assumed, such as that acquired in the first year of an Honours Chemistry course. A Glossary of some fundamental terms has been included in order to help readers with limited background knowledge. Lists of Further Reading direct the reader to fuller accounts of certain areas and also provide him/her with an introit into more detailed or advanced treatments. The material of the book should in turn provide a basis from which specialised final-year courses can be developed, either in pure chemistry or in one of the ever-increasing number of joint or combined degree courses.

The list of grateful thanks to some of the many people who have helped in various ways to guide this book from inception to publication should start with Bob Gillard, Professor at University College Cardiff. It was his invitation to survey the current state of this area of chemistry at the RSC Autumn Meeting held at University College Cardiff in 1980 which led to a series of lectures around the country. This in turn, specifically the lecture at Hull, led to the suggestion of the preparation of a cassette

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and workbook. I am grateful to Dick Moyse for initiating and encouraging this idea, and to Peter Groves for his subsequent enthusiasm and patience in coaxing the first cassette into being. I am very grateful both to Peter Groves and to Ellis Horwood my publishers for their cooperation in arranging for parallel production of this textbook, and to Ellis himself and his experienced and dedicated staff for all their efforts and care in its preparation. Finally it gives me pleasure to acknowledge my debt to my colleagues at Leicester and to several generations of undergraduates and research students there, whose support, interest, and enquiring minds have done so much to improve my knowledge of chemistry, in solution and indeed in general.

Leicester
December 1987

John Burgess

List of symbols and abbreviations

|	
aq	water; aquated; aqueous medium
C	heat capacity (specific heat)
	C_P isobaric (constant pressure) heat capacity
	$\Delta C_P^{\ddagger}$ heat capacity of activation
CFAE	crystal field activation energy
CFSE	crystal field stabilisation energy
d^n	d-electron configuration of a transition metal ion
D	dissociative (mechanism)
Dq	crystal field splitting parameter
E	energy; redox potential
	$E^{\ominus}$ standard redox potential
e_g	see Glossary, under 'Crystal Field'
EXAFS	extended X-ray absorption fine structure
$\mathscr{F}$	Faraday
$g(r)$	radial distribution function
G	Gibbs free energy
	$\Delta G^{\ominus}$ standard Gibbs free energy change
	$\Delta G^{\ddagger}$ Gibbs free energy of activation
h	Planck's constant
H	enthalpy
	ΔH_{hydr} enthalpy of hydration
	$\Delta H^{\ddagger}$ enthalpy of activation
	$\Delta H(\text{M–L})$ metal–ligand bond dissociation energy
HSAB	Hard and Soft Acids and Bases
I	interchange mechanism
I_a	associative interchange
I_d	dissociative interchange
k	rate constant
	k_0 rate constant at atmospheric pressure
	k_1 first-order rate constant (dissociative or solvolysis path)

k_2		second-order rate constant (associative path)
k_b		rate constant for reverse (back) reaction in an equilibrium
k_{ex}		rate constant for solvent (ligand) exchange
k_f		rate constant for complex formation *or* rate constant for forward reaction in an equilibrium
k_P		rate constant at high pressure
K		equilibrium constant (see also pK below)
	K_n	stability constant for the addition of the nth ligand in complex formation
	K_{os}	outer-sphere association constant
n		number of ligands in a complex *or* number of electrons
P		pressure
pK		negative logarithm to base 10 of equilibrium (stability) constant K (analogous to pH)
R		alkyl
R		gas constant
S		entropy
	$S^{\ominus}$	standard partial molar entropy
	$\Delta S^{\ddagger}$	entropy of activation
SCS		sterically controlled substitution (mechanism)
S_N		nucleophilic substitution
	S_N1	unimolecular, i.e. dissociative
	$S_N1(\text{lim})$	limiting dissociative mechanism
	S_N2	bimolecular, i.e. associative
T		temperature
t_{2g}		see Glossary, under 'Crystal Field'
V		volume
	$\bar{V}^{\ominus}$	standard partial molar volume
	$\Delta V^{\ddagger}$	volume of activation
	$\Delta V_i^{\ddagger}$	volume of activation for ligand interchange
	$\Delta V^{\ominus}$	standard volume change for a reaction
	$\Delta V_{os}^{\ominus}$	standard volume change for outer-sphere pre-association equilibrium
w_{ij}		work term (in bringing reactants, particularly in redox reactions, together)
z		charge on an ion
β_n		stability constant for the addition of n ligands to a metal ion
ν		frequency

ABBREVIATIONS FOR LIGANDS AND SOLVENTS

Lower-case letters are used in this book for ligand abbreviations, upper-case for solvent abbreviations. Such compounds as dimethyl sulphoxide can act in either capacity: their typographical appearance varies accordingly.

Ligands which are anions of weak acids are taken as L^{n-}: the free organic molecule is then LH_n.

aa^-	amino-acid anion (see ala^-, asp^-, gly^-)	
$acac^-$	acetylacetonate(pentane-2,4-dionate)	$[MeCOCHCOMe]^-$
ala^-	alaninate	$[MeCH(NH_2)CO_2]^-$
asp^-	aspartate	$[HO_2CCH_2CH(NH_2)CO_2]^-$
bipy	2,2'-bipyridyl	
$3CNacac^-$	3-cyanoacetylacetonate	$[MeCOC(CN)COMe]^-$
cp^-	cyclopentadienyl anion	
DMA	NN-dimethylacetamide	$MeCONMe_2$
DMF/dmf	NN-dimethylformamide	$HCONMe_2$
DMSO/dmso	dimethyl sulphoxide	Me_2SO
$edta^{4-}$	ethylenediaminetetraacetate (ethane-1,2-di-aminetetraacetate)	
en	ethylenediamine (ethane-1,2-diamine)	$H_2NCH_2CH_2NH_2$
gly^-	glycinate	$[H_2NCH_2CO_2]^-$
HMPA/hmpa	hexamethylphosphor(tri)amide	$OP(ONMe_2)_3$
L,LL,LLL,..	general symbols for mono-, bi-, tri-dentate ligand	
4,7-Me_2phen	4,7-dimethyl-1,10-phenanthroline	
Nu, nucl	nucleophile	
ox^{2-}	oxalate	$[O_2CCO_2]^{2-}$
oxinate	8-hydroxyquinolinate	
pada	pyridine-2-azo-4'-dimethylaniline	
PC	propylene carbonate (4-methyl-1,3-dioxalan-2-one)	
phen	1,10-phenanthroline	
py	pyridine	
terpy	2,2',6',2''-terpyridyl	
THF	tetrahydrofuran	
TMP	trimethyl phosphate	$OP(OMe)_3$
TMTU	tetramethylthiourea	$SC(NMe_2)_2$
TMU	tetramethylurea	$OC(NMe_2)_2$
tu	thiourea	$SC(NH_2)_2$
X^-	halide	

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Introduction

1.1 DISSOLUTION OF SALTS

One of the best ways to appreciate the importance of ion–solvent interactions in electrolyte solutions is through the cycle shown as the top half of Fig. 1.1. This relates

$$\text{MX(crystal)} \xrightarrow{\begin{array}{c}\text{enthalpy}\\\text{of solution}\end{array}} \text{M}^+\text{(solv)} + \text{X}^-\text{(solv)}$$

Lattice enthalpy

sum of ion solvation enthalpies

$$\text{M}^+\text{(g)} + \text{X}^-\text{(g)}$$

Na$^+$(g) + Cl$^-$(g)

ΔH (kJ mol^{-1})

784

788

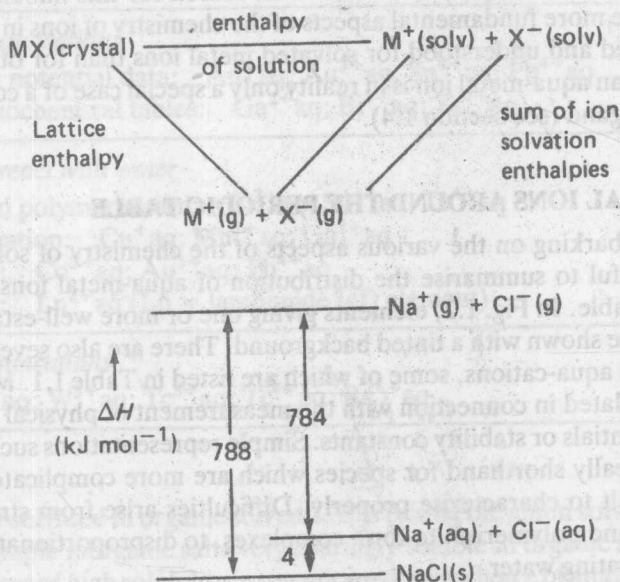Na$^+$(aq) + Cl$^-$(aq)

4

NaCl(s)

Fig. 1.1 — Interrelation of solution, solvation, and lattice enthalpies.

the enthalpy of solution to ion solvation enthalpies and to lattice enthalpy. Invariably the enthalpy of solution of a salt is the small difference between the large enthalpy needed to separate the ions from each other in the crystal lattice and the enthalpy

gained when these ions are introduced into the solvent. The lower half of Fig. 1.1 shows that for the specific case of sodium chloride, the enthalpy of solution is only about 0.5% of the lattice or ion solvation enthalpies. Fig. 1.1 should give some idea of the strength of ion–solvent, particularly ion–water, interactions. In the following pages various aspects of the chemistry of solvated ions — their natures, properties, and reactions — are introduced.

Solvent molecules can become attracted to ions with varying degrees of firmness, depending of course on the characteristics of both the ion and the solvent. The introduction of ions into a solvent can also have a marked effect on its properties. This is particularly true when, as in the case of water, the solvent has a pronounced structure of its own. Indeed the commonest and most important solvent, water, is one of the most interesting in this respect, since in aqueous solutions of salts interactions between ions and solvent molecules profoundly affect interactions between the solvent molecules themselves. Many sections will deal mainly with aqueous solutions, as these have received most attention, owing both to the importance of water and to its interest as a solvent. However, the study of non-aqueous solvents has developed greatly in some areas, and such solutions will be discussed where appropriate.

Much of this book, especially the earlier chapters, will be concerned with the nature and properties of metal ions, though much of the discussion is equally relevant to anions and to complex ions. The main reason for this imbalance is simply that some of the more fundamental aspects of the chemistry of ions in solution are better documented and understood for solvated metal ions than for other solute species. However, an aqua-metal ion is in reality only a special case of a complex with water acting as ligand (see section 1.4).

1.2   METAL IONS AROUND THE PERIODIC TABLE

Before embarking on the various aspects of the chemistry of solvated ions, it may prove helpful to summarise the distribution of aqua-metal ions in relation to the Periodic Table. In Fig. 1.2, elements giving one or more well-established species of this type are shown with a tinted background. There are also several much less well-established aqua-cations, some of which are listed in Table 1.1. Many of these have been postulated in connection with the measurement of physical properties such as redox potentials or stability constants. Simple representations such as Au^+, Bi^{3+}, or Zr^{4+} are really shorthand for species which are more complicated and indeed are very difficult to characterise properly. Difficulties arise from strong tendencies to hydrolyse and polymerise, to form complexes, to disproportionate, or to oxidise or reduce solvating water.

Salts dissolve to a greater or lesser extent in a range of polar solvents, both hydroxylic solvents such as the alcohols and dipolar aprotic solvents such as acetonitrile or dimethyl sulphoxide. In all these cases the cations will be solvated, as in aqueous solution. Methanol, ethanol, and acetone are rather less effective in solvating metal ions than water, but dimethyl sulphoxide or pyridine solvate some cations considerably more effectively than water. In general metal ions which give hydrated cations in water can usually give analogous solvated cations in polar organic solvents. Simple inorganic anions, on the other hand, such as halides or oxoanions,