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IONS IN SOLUTION (I)

John Burgess

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IONS IN SOLUTION (I)

JOHN BURGESS

John Burgess read Natural Sciences at the University of Cambridge, and went on to obtain his PhD degree there in inorganic reaction kinetics with Dr R H Prince. After two years with Fisons Fertilizers he became an ICI Research Fellow at the University of Leicester, working with Professor M C R Symons. He was then appointed to a Lecturership in Inorganic Chemistry at Leicester, subsequently becoming Senior Lecturer.

His interests remain centred on inorganic kinetics and mechanisms but include related areas of thermo-chemistry and charge-transfer spectroscopy. His current research is mainly concerned with elucidating the effects of solvent and of pressure, and rationalising these in terms of solvation changes - both between various media and between initial (ground) and transition (excited) states.

Dr Burgess has been chronicling the progress of inorganic chemistry for many years, starting with contributions to Annual Reports for 1966. He started the Chemical Society's Specialist Periodical Report on this area in 1970 and continued to contribute until its demise. Since then he has been involved in the establishment of its successor under the aegis of Plenum Press. He has written numerous articles and reviews on his areas of research interest; the book 'Metal Ions in Solution' from which this Chemistry Cassette derives; and has recently contributed to Gmelin's two volume coverage of the chemistry of technetium.

CHEMISTRY CASSETTES

General Editor: **Peter Groves**

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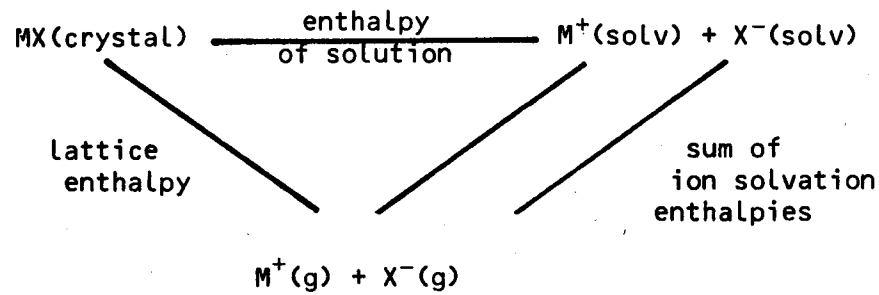
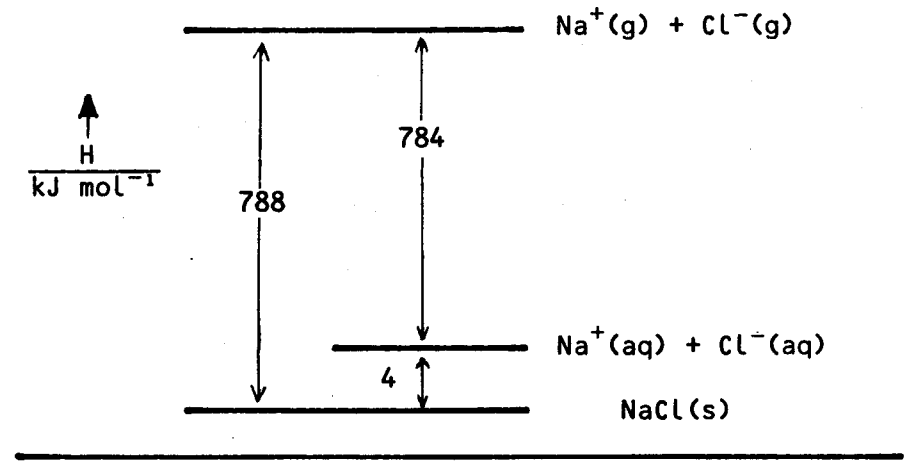
A glossary of some of the scientific and technical terms used in this programme will be found on page 37.

1 INTERRELATION OF SOLUTION, SOLVATION AND LATTICE ENERGIES





2

TOPICS TO BE COVERED

Introduction
- Dissolution of salts
- Metal ions around the Periodic Table
- New aquo-metal ions
- Model for ions in solution

Solvation numbers
- N.m.r spectroscopy
- Ion-movement methods
- Review of solvation numbers

Ion-solvent distances
- X-ray diffraction
- Results

Ion-solvent interactions
- Ultraviolet-visible spectroscopy
- Infra red-Raman spectroscopy

Hydrolysis and polymerization
- pK values for aquo-cations
- Hydroxo-bridged polynuclear species

3

DISTRIBUTION OF THE ELEMENTS WHICH GIVE ONE OR MORE WELL-ESTABLISHED SOLVATED CATION SPECIES

(Such elements are indicated by a grey background)

H																	He
Li	Be												B	C	N	O	F	Ne
Na	Mg												Al	Si	P	S	Cl	Ar
K	Ca	Sc		Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y		Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Ln†	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Act††															

† Lanthanide cations
†† Actinide cations

4

A. ILL-CHARACTERIZED AQUO-CATIONS

Hypothetical redox species: $Au^{+}aq$, $Au^{3+}aq$, $Sn^{4+}aq$, $Pb^{4+}aq$
Hypothetical thermochemical species: $Ga^{2+}aq$, $Bi^{3+}aq$, $Zr^{4+}aq$

DIFFICULTIES IN CONNECTION WITH THESE

Hydrolysis and polymerization: $Sn^{4+}aq$, $Bi^{3+}aq$, $Zr^{4+}aq$
Disproportionation: $Ga^{2+}aq$, $Cu^{+}aq$
Redox reaction with water: $Au^{3+}aq$, $Pb^{4+}aq$, $Lanth^{2+}aq$

B. POSSIBLE FUTURE AQUO-CATIONS

$W^{3+}aq$, $Tc^{3+}aq$, $Tc^{4+}aq$, $Re^{4+}aq$
$Os^{2+}aq$, $Os^{3+}aq$, $Os_2^{n+}aq$

5 RECENT AQUO-METAL IONS

MOLYBDENUM(III) (1975)

$$MoCl_6^{3-} \xrightarrow[\text{HPTS or } HBF_4]{O_2\text{-free}} Mo^{3+}aq$$

IRIDIUM(III) (1976)

$$IrCl_6^{2-} \xrightarrow{0.1M\ NaOH} \text{hydroxo-iridium(III)} + O_2$$

$$\downarrow \begin{array}{l} 1\ \text{ascorbic acid} \\ 2\ \text{pH 8 } (HClO_4) \end{array}$$

$$Ir(OH)_3aq$$

$$\downarrow 0.1M\ HClO_4$$

$$Ir^{3+}aq$$

$$[\text{contrast } RhCl_6^{3-} \xrightarrow[\text{boil}]{c.HClO_4} Rh^{3+}aq]$$

PLATINUM(II) (1976)

$$PtCl_4^{2-} \xrightarrow[\substack{AgClO_4 \text{ or } Hg(ClO_4)_2 \\ 6\ \text{days. } 70^oC}]{} Pt^{2+}aq$$

$$[\text{contrast } Pd^{2+}aq]$$

6 RHENIUM(IV) AND PLATINUM(IV)

$$ReCl_6^{2-} \xrightarrow[\substack{HClO_4 \\ \text{(no air)}}]{Hg(ClO_4)_2} Re^{4+}aq$$

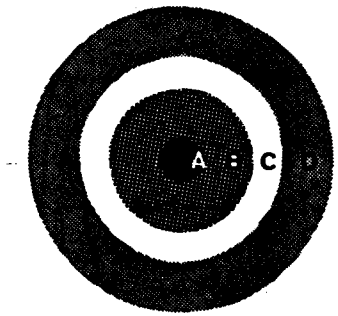
$$Pt^{2+}aq \xrightarrow{Cl_2} Pt(OH_2)_5Cl^{3+} \xrightarrow{Ag^+ \text{ or } Hg^{2+}} Pt^{4+}aq$$

7 EPHEMERAL AQUO-CATIONS

Chemical generation: $Co^{3+}aq$, $Cu^{+}aq$

From pulse radiolysis: $Zn^{+}aq$, $Cd^{+}aq$, $Ni^{+}aq$

8 THE ENVIRONMENT OF AN ION IN AQUEOUS SOLUTION



A. primary solvation shell
B. secondary solvation shell
C. disordered region
D. bulk solvent

9 METHODS FOR ESTIMATING SOLVATION NUMBERS FOR IONS

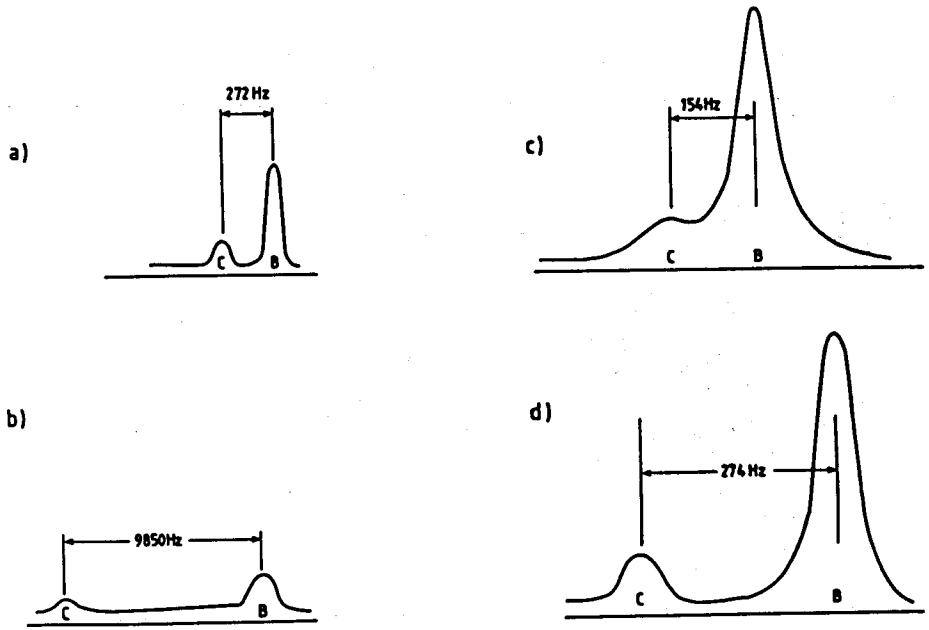
Spectroscopic
- n.m.r.
- ultraviolet-visible
- infra red-Raman

Transport properties
- transference numbers
- ionic conductances
- mobilities
- viscosities

Thermochemical
- entropies
- volumes
- compressibilities

Other methods
- isotopic dilution
- dielectric constants

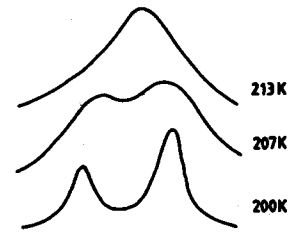
10 PROTON N.M.R. SPECTRA



Proton n.m.r. spectra of aqueous solutions of
(a) gallium(III) perchlorate (1.29M; 211K),
(b) cobalt(II) perchlorate (3.2M; 213K),
(c) indium(III) chloride (3.81M; 213K).
Proton n.m.r spectrum of 1:5 aqueous acetone solution of
(d) indium(III) perchlorate (0.11M; 173K).

The signals marked C arise from cation primary hydration; those marked B from the remaining water molecules in the system.

11 VARIATION OF ^1H N:M:R: SPECTRA WITH TEMPERATURE FOR THE Mg^{2+} CATION IN MAGNESIUM PERCHLORATE SOLUTION IN AQUEOUS ACETONE



12 CATION SOLVATION NUMBERS DETERMINED BY N.M.R. PEAK AREA TECHNIQUES

	Water	Ammonia	Methanol	Ethanol	Acetonitrile	DMF	DMSO
sp-elements							
Be^{2+}	4					4	
Mg^{2+}	6	6	6				
Zn^{2+}	6		6				
Al^{3+}	6	6	6	6		6	6
Ga^{3+}	6		6		6	6	
In^{3+}	6						
transition elements							
Fe^{2+}	6						
Co^{2+}	6		6		6	6	6
Ni^{2+}	6		(5)				6
Pt^{2+}	4						
actinides							
Th^{4+}	9						

13 IONIC MOBILITIES FOR METAL IONS AND FOR HALIDES IN AQUEOUS SOLUTION AT 298.2K

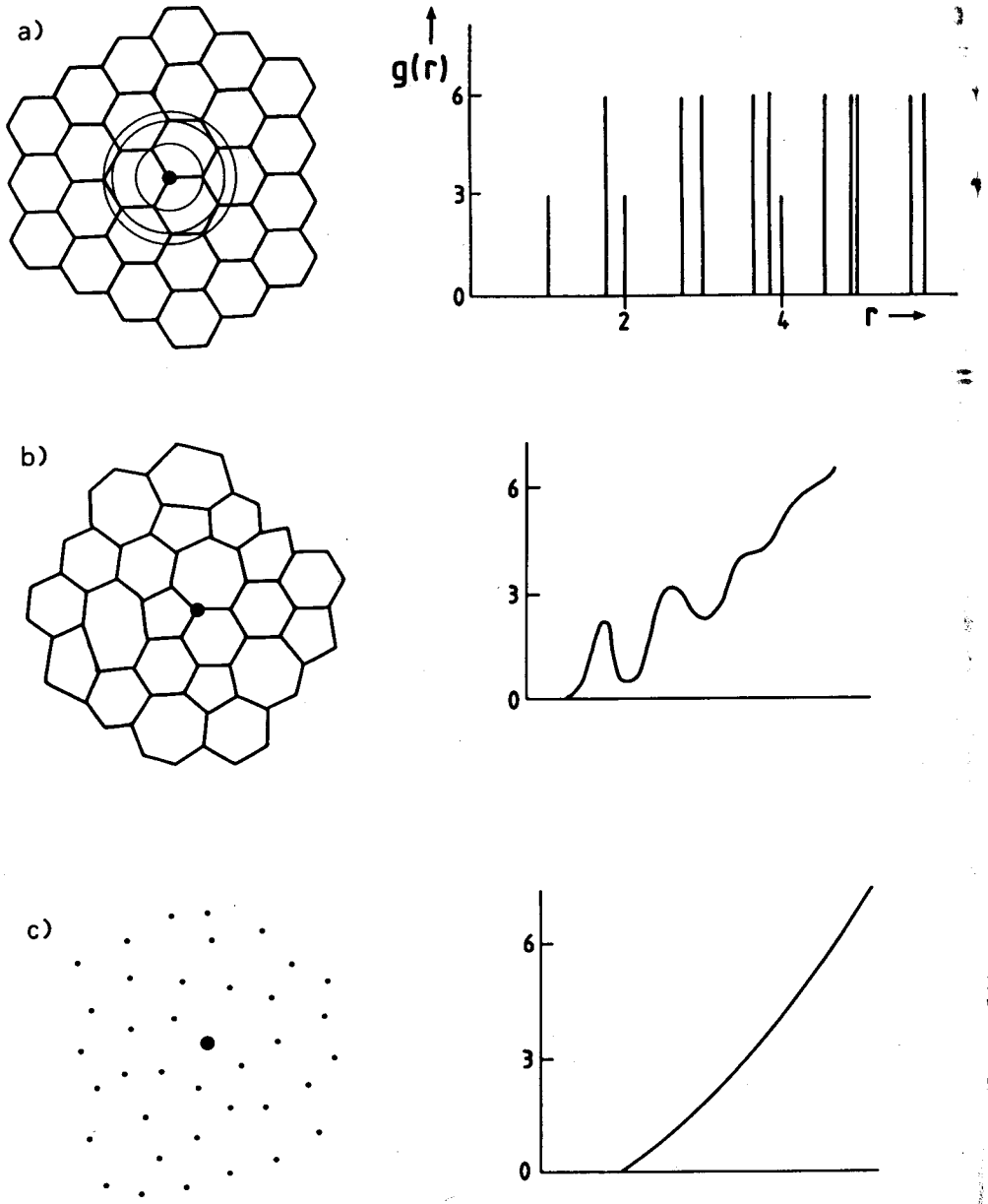
Li^{+}	4.01	Ca^{2+}	6.17	F^{-}	5.70
Na^{+}	5.19	Ba^{2+}	6.60	Cl^{-}	7.91
K^{+}	7.61			Br^{-}	8.13
Rb^{+}	7.92	Cu^{2+}	5.60	I^{-}	7.95
Ag^{+}	6.42	La^{3+}	7.21	SO_4^{2-}	8.27

Values have been multiplied by 10^4 and are in $cm^2\ s^{-1}\ V^{-1}$.

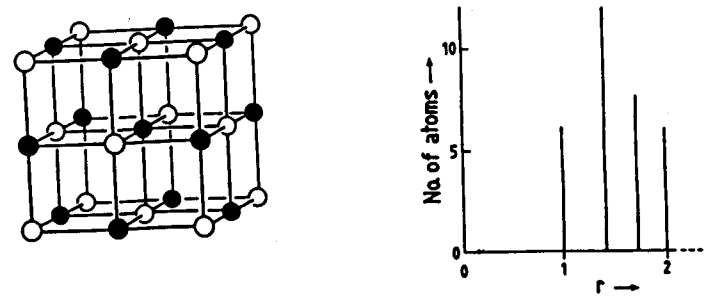
CATION HYDRATION NUMBERS

	Li^+	Na^+	K^+	Cs^+	Mg^{2+}	Ca^{2+}	Ba^{2+}	Zn^{2+}	Fe^{2+}	Al^{3+}	Cr^{3+}	
transference numbers	13-22	7-13	4-6	4	12-14	8-12	3-5	10-13				transference numbers
mobilities	3-21	2-10	5-7		10-13	7-11	5-9	10-13	10-13			mobilities
conductivities	2-3	2-4		6	8	8	8					conductivities
diffusion	5	3	1	1	9	9	8	11	12	13	17	diffusion
entropies	5	4	3	3	13	10	8	12	12	21		entropies
compressibilities	3	4	3							31		compressibilities
activity coefficients					5	4	3		12	12		activity coefficients
cf. n.m.r. peak areas					6			6	6		6	cf. n.m.r. peak areas

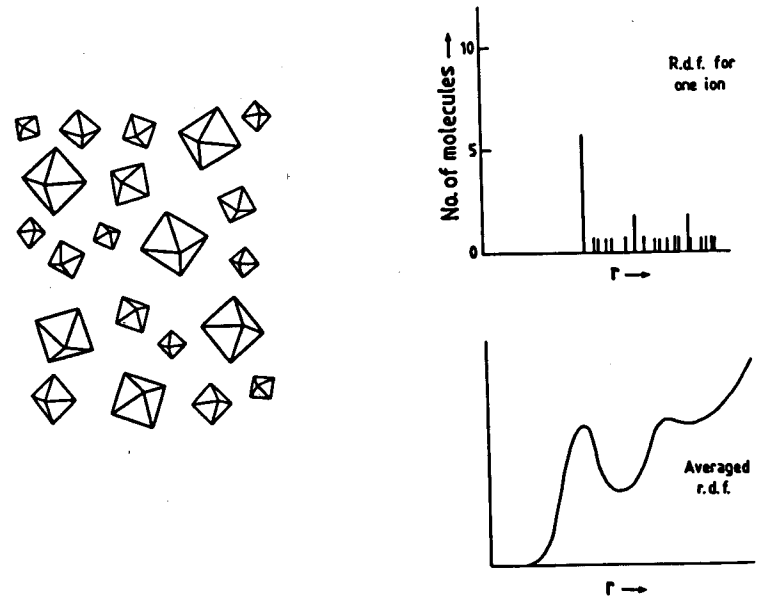
15 TWO-DIMENSIONAL RADIAL DISTRIBUTION FUNCTIONS



16 THREE-DIMENSIONAL RADIAL DISTRIBUTION FUNCTIONS



(a) sodium chloride structure



(b) hexasolvento-ions in solution

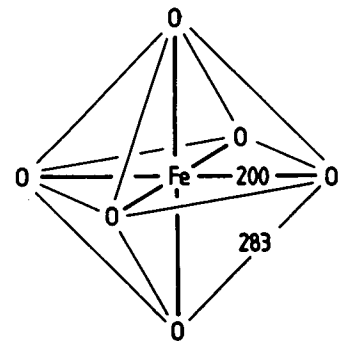
17 METAL ION TO OXYGEN DISTANCES IN AQUO-CATIONS

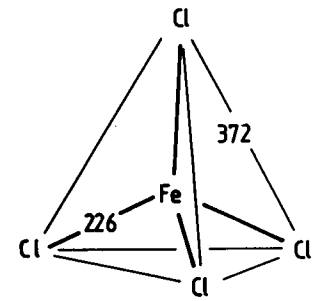
All distances are in pm. Distances from X-ray diffraction and neutron diffraction studies on aquo-cations in solution are compared with those in crystal hydrates and with ionic radii (for six coordination).

	Aqueous solution		Crystal hydrates	Ionic radii
	X-ray diffrn.	Neutron diffrn.		
Na^+	240†	250	235-252	116
Ag^+	243†			129
Mg^{2+}	210		201-214	86
Ca^{2+}	240	240	230-249	114
Mn^{2+}	220		200	96
Fe^{2+}	212		208	91
Co^{2+}	208		193-212	88
Ni^{2+}	204	207	202-211	84
Cu^{2+}	194¶		193-200	87
	243¶		¤	
Zn^{2+}	208		208-214	89
Cd^{2+}	231		224-231	109
Al^{3+}	190		187	67
In^{3+}	215		223	93
Cr^{3+}	194		202	76

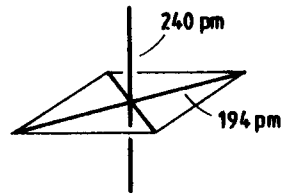
† Na^+ environment tetrahedral, Ag^+ linear, rest octahedral.
¶ Cu^{2+} has a tetragonal environment (see frame 19).
¤ It is difficult to find the solid state equivalent: $Cu(ClO_4)_2.6H_2O$ has two waters at 209pm, two at 216pm, two at 228pm.

18 PRIMARY SOLVATION SHELL GEOMETRIES

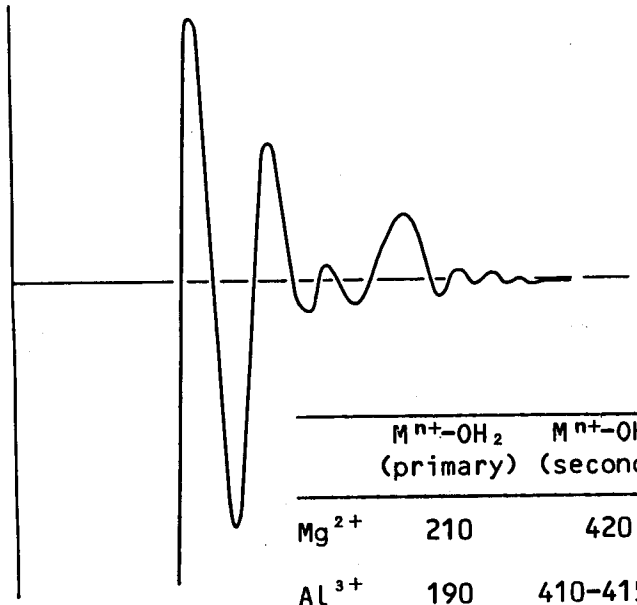




19 TETRAGONAL DISTORTION IN $Cu(OH_2)_6^{2+}$



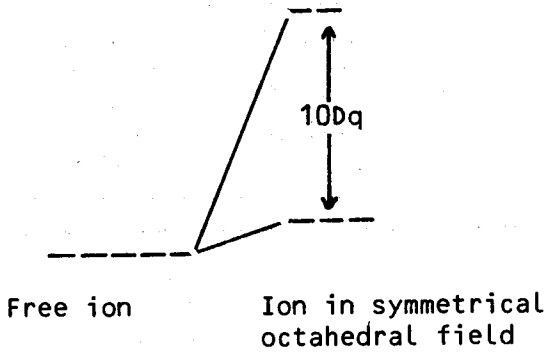
20 PRIMARY AND SECONDARY CATION HYDRATION FROM X-RAY DIFFRACTION

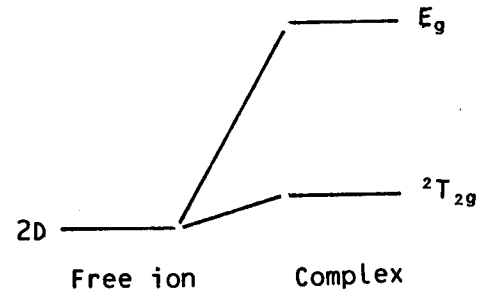


	$M^{n+}-OH_2$ (primary)	$M^{n+}-OH_2$ (secondary)
Mg^{2+}	210	420
Al^{3+}	190	410-415
Cr^{3+}	198	420-425
Fe^{3+}	204	410-415

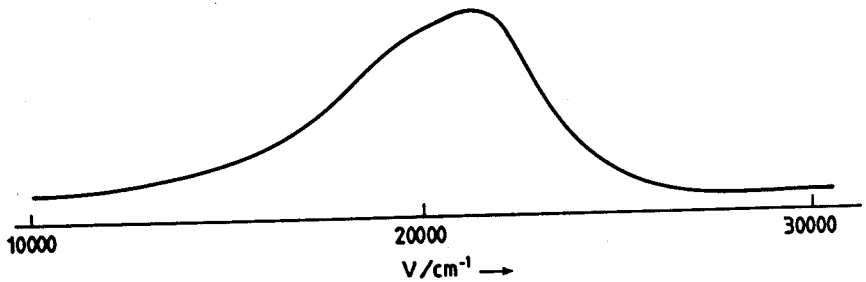
Metal-oxygen distances in pm.

21 EFFECT OF LIGAND (SOLVENT) COORDINATION ON THE d LEVELS AND ^2D TERM OF A TRANSITION METAL CATION





22 ULTRAVIOLET-VISIBLE SPECTRUM OF $Ti^{3+}aq$ IN AQUEOUS SOLUTION



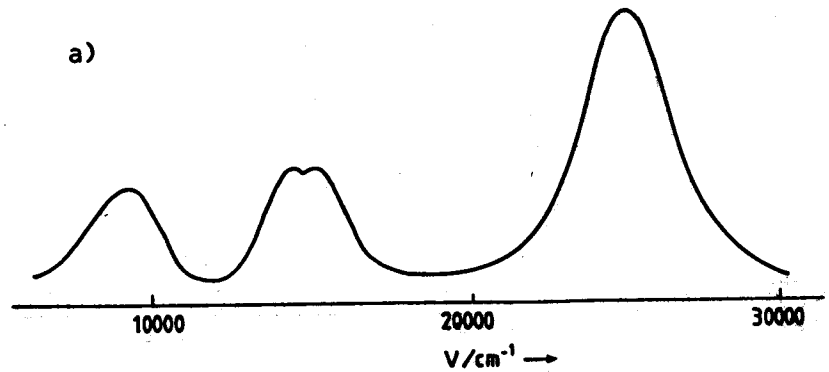
23 WAVENUMBERS OF MAXIMUM ABSORPTION FOR Ti^{3+} IN WATER AND ALCOHOLS

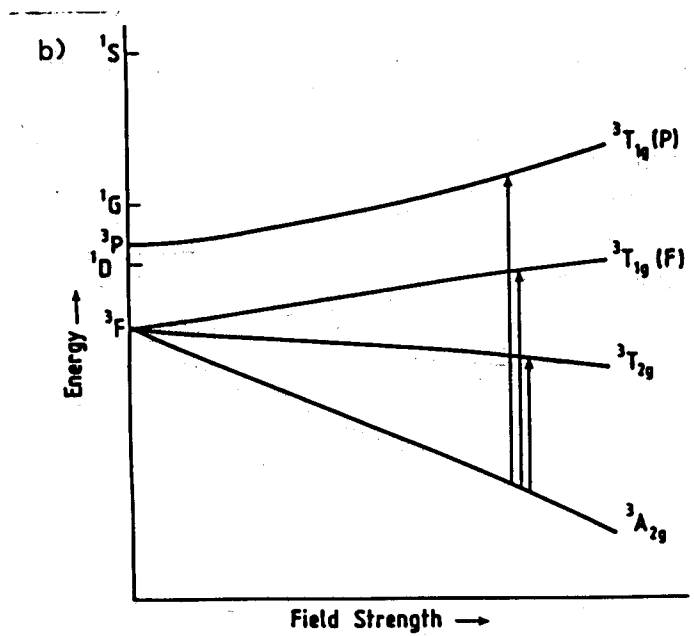
solvent	ν_{max}/cm^{-1}
water	20080
methanol	16850
ethanol	16750

24

a) ABSORPTION SPECTRUM OF $Ni^{2+}aq$

b) THE THREE TRANSITIONS INVOLVED IN THE ABSORPTION OF A d^8 CATION, e.g. $Ni^{2+}aq$ IN AN OCTAHEDRAL LIGAND FIELD





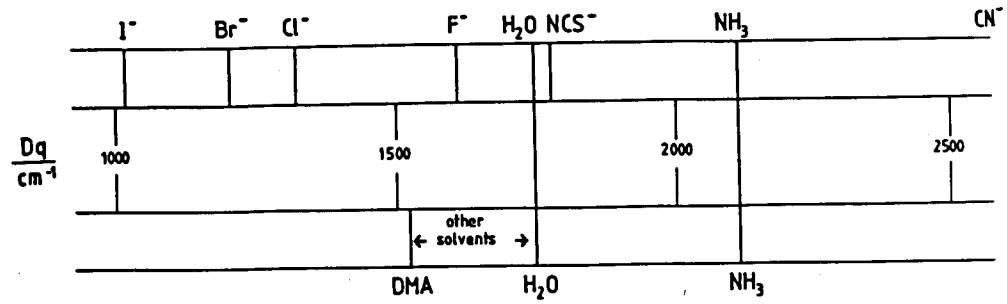
25 VALUES OF THE CRYSTAL FIELD SPLITTING PARAMETER, Dq/cm^{-1}, FOR TRANSITION METAL CATIONS IN AQUEOUS SOLUTION

d^1			Ti^{3+}	2030		
d^2			V^{3+}	1860		
d^3	V^{2+}	1230	Cr^{3+}	1700	Mo^{3+}	2630
d^4	Cr^{2+}	1410	Mn^{3+}	2000		
d^5	Mn^{2+}	850	Fe^{3+}	~1400		
d^6	Fe^{2+}	1000	Co^{3+}	1820	Rh^{3+}	~2700
d^7	Co^{2+}	930				
d^8	Ni^{2+}	890				
d^9	Cu^{2+}	1200				

26 DEPENDENCE OF CRYSTAL FIELD SPLITTING PARAMETER, Dq/cm^{-1}, ON NATURE OF SOLVENT

	Co^{2+}	Ni^{2+}	Cr^{3+}
NN-dimethylacetamide	805	796	1538
dimethyl sulphoxide	840	777	1587
trimethyl phosphate	975	796	1628
ethanol			1668
methanol		850	1695
NN-dimethylformamide		850	1710
water	1000	875	1720
acetonitrile	1022	1026	
liquid ammonia	1010	1080	2155

27 CORRELATION OF SOLVENT AND LIGAND SPECTROCHEMICAL SERIES FOR CHROMIUM(III)

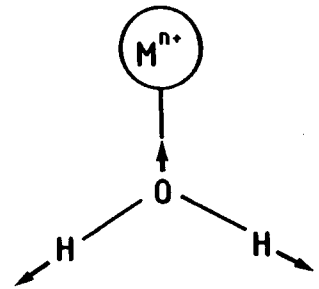


28 EXERCISE

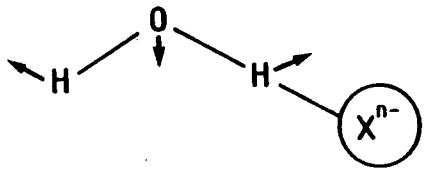
Study frames 25, 26 and 27. What trends can you discern in the data?

Try to relate these trends to (i) size, charge and d electron configuration of the cations, and (ii) basicity and σ-donor ability of the solvents.

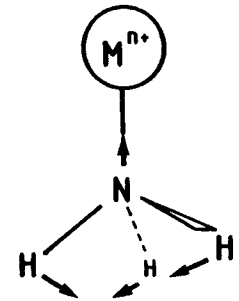
29 THE RELATION OF MODES OF VIBRATION OF SOLVENT MOLECULES TO THEIR COORDINATION TO CATIONS



(a) for water



(b) for water



(c) for ammonia

30 PERTURBATION OF SOLVENT VIBRATIONS BY METAL IONS - I

The effects of cations on the vibrational frequency, ν_1, of solvating water:

$Ce^{4+} > Al^{3+} > Ba^{2+} > Mg^{2+} \sim Li^{+} > Na^{+} \sim K^{+}$

31 PERTURBATION OF SOLVENT VIBRATIONS BY METAL IONS - II

The effects of cations on the stretching frequencies of acetonitrile:

	$\Delta\nu(C-C)/cm^{-1}$	$\Delta\nu(C\equiv C)/cm^{-1}$
Li^{+}	+15	+22
Na^{+}	+8	+12
K^{+}	+6	+10
Rb^{+}	+5	+9
Cs^{+}		+9
Mg^{2+}	+20	+37
Co^{2+}	+18	+35
$Ru(NH_3)_5^{2+}$		-15
$Ru(NH_3)_5^{3+}$		+32

32 METAL ION - SOLVENT VIBRATIONAL FREQUENCIES (cm^{-1})

This table illustrates their dependence on the nature of the ion and of the solvent, including isotope effects (H_2O vs. D_2O).

	water H_2O	water D_2O	liquid ammonia	DMSO	acetone	THF	propylene carbonate
Li^+				429	420-425	412-413	397
Na^+			194	195-206	195-196	175-198	186
K^+				153-154	148	142	144
Cs^+				109-118			112
Ag^+			260-263				
Be^{2+}	530-543		485				
Mg^{2+}	360-365	344	328-330				
Ba^{2+}			215				
Zn^{2+}	385-400		435-440				
Al^{3+}	520-526	503					
Ga^{3+}	475		477				
In^{3+}	400		440				

33 HYDROLYSIS AND POLYMERIZATION

(a) hydrolysis or proton loss:

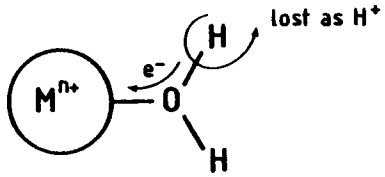
$$M(OH)_x^{n+} \rightleftharpoons M(OH_2)_{x-1}(OH)^{(n-1)+} + H^+aq$$

e.g. $Al(OH_2)_6^{3+} \rightleftharpoons Al(OH_2)_5(OH)^{2+} + H^+aq$

(b) e.g. $2Al(OH)^{2+}aq \rightleftharpoons [Al\langle^{OH}_{OH}\rangle Al]^{4+}aq$

(c) mercurous ion, $Hg_2^{2+}aq \equiv [Hg - Hg]^{2+}aq$

34 ACIDITY OF SOLVATED CATIONS



35 EQUILIBRIUM CONSTANTS RELATING TO ACIDITY OF AQUO-CATIONS

(a) $M^{n+} + OH^- = M(OH)^{(n-1)+}$ $\qquad K_1 = \frac{[M(OH)^{(n-1)+}]}{[M^{n+}][OH^-]}$

(b) $M^{n+} + H_2O = M(OH)^{(n-1)+} + H_3O^+$ $\qquad {}^*K_1 = \frac{[M(OH)^{(n-1)+}][H_3O^+]}{[M^{n+}][H_2O]}$

Notes: (i) equation (b) is equivalent to frame 33(a)
(ii) ${}^*K_1/K_1 = K_w$; K_h defined as $1/{}^*K_1$
(iii) $p{}^*K_1 = -\log_{10} {}^*K_1$, etc.
(iv) $[H_2O]$ put at one in ${}^*K_1$
(v) we shall use ${}^*K_1$ (rather than K_1) here.

36 SELECTED VALUES OF $p{}^*K_1$ FOR AQUO-METAL IONS

Values are at 298.2K, on the molar scale, and where possible refer to zero ionic strength. Values in brackets are very approximate.

sp-block elements

Li^+	13.9	Mg^{2+}	11.4	Al^{3+}	5.0	Po^{4+}	(1?)
Na^+	14.7	Ca^{2+}	12.6	Sc^{3+}	(5)		
		Sr^{2+}	13.1	Y^{3+}	(8)		
Tl^+	13.3	Ba^{2+}	13.3	La^{3+}	(9)		
Ag^+	11.9						
		Zn^{2+}	9.5	Ga^{3+}	2.6		
		Cd^{2+}	7.9	Tl^{3+}	(1)		
		Sn^{2+}	1.9				

transition metals

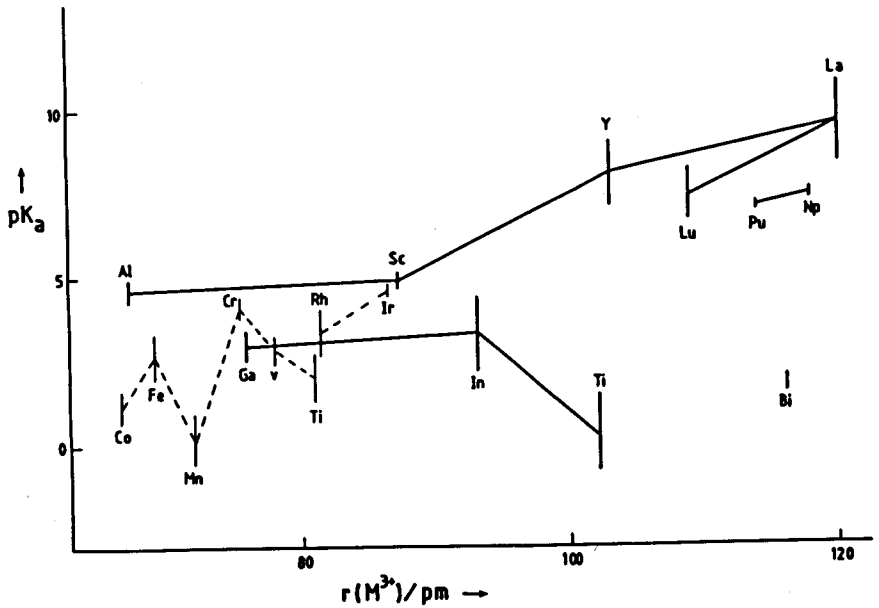
Cr^{2+}	9	Cr^{3+}	3.9
Fe^{2+}	(7)	Fe^{3+}	2.0
Ni^{2+}	10		
Pd^{2+}	1.4		

lanthanides and actinides

Ce^{3+}	9.3	Ce^{4+}	(0)
Gd^{3+}	8.6		
Lu^{3+}	8		
		U^{4+}	1
Pu^{3+}	7.0	Pu^{4+}	1.5

37 ACIDITY OF AQUO-CATIONS

Examination of the relation between p^*K_1 and cation radius for 3+ metal ions.



38 AQUO-CATIONS: LOSS OF MORE THAN ONE PROTON

(a) Successive proton loss from different water molecules:

eg $M(OH_2)_6^{3+} \overset{K_1}{\rightleftharpoons} M(OH_2)_5(OH)^{2+} + H^+ \overset{K_2}{\rightleftharpoons} M(OH_2)_4(OH)_2^{+} + H^+ \overset{K_3}{\rightleftharpoons}$ etc.

(b) Loss of two protons from one solvating water molecule:

eg "$V(OH_2)^{4+}$" $\xrightarrow{-2H^+}$ VO^{2+}

or twice over

eg "$U(OH_2)_2^{6+}$" $\xrightarrow{-4H^+}$ UO_2^{2+}

(c) Loss of all protons from solvating water molecules:

eg "$V(OH_2)_3^{5+}$" $\xrightarrow{-6H^+}$ VO_3^-

39 INTERRELATION OF AQUO-CATIONS, HYDROXO-CATIONS, POLYNUCLEAR CATIONS, HYDROXIDES AND METALLATES

ALUMINIUM(III)

$Al^{3+}aq \rightleftharpoons Al(OH)^{2+}aq \longrightarrow Al(OH)_3 \longrightarrow AlO_2^-$

$\rightleftarrows Al_2(OH)_2^{4+}$

$\rightleftarrows Al_3(OH)_4^{5+}$

$\rightleftarrows Al_8(OH)_{20}^{4+}$

$\rightleftarrows Al_{13}O_4(OH)_{24}^{7+}$

BISMUTH(III)

$Bi^{3+}aq(?) \rightleftharpoons Bi(OH)^{2+}aq(?) \longrightarrow Bi(OH)_3$

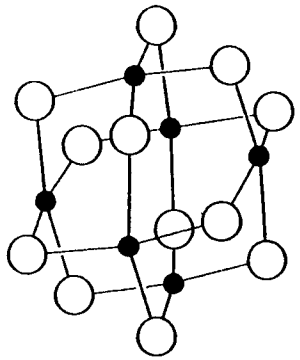
$\rightleftarrows Bi_2(OH)_4^{2+};\ Bi_2(OH)_5^{+}$

$\rightleftarrows Bi_4O_4^{4+};\ Bi_4O_3(OH)_4^{2+}$

$\rightleftarrows Bi_6O_6^{6+};\ Bi_6(OH)_{12}^{6+}$

$\rightleftarrows Bi_8O_{10}^{4+}$

$\rightleftarrows Bi_9(OH)_{20}^{7+};\ Bi_9(OH)_{21}^{6+};\ Bi_9(OH)_{22}^{5+}$

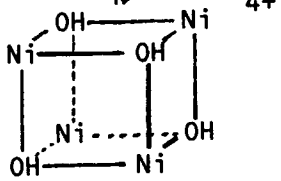


NICKEL(II)

$Ni^{2+}aq \rightleftharpoons Ni(OH)^{+}aq \longrightarrow Ni(OH)_2$

$\rightleftarrows Ni_2(OH)^{3+}$

$\rightleftarrows$



LEAD(II)

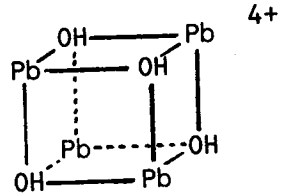
$Pb^{2+}aq \rightleftharpoons Pb(OH)^{+}aq \longrightarrow Pb(OH)_2$ - plumbites

$\rightleftarrows Pb_2(OH)^{3+}$

$\rightleftarrows Pb_3(OH)_4^{2+}$

$\rightleftarrows Pb_4(OH)_4^{4+}$

$\rightleftarrows Pb_6(OH)_8^{4+}$



GLOSSARY

You may not be familiar with all the scientific and technical terms used in this cassette and workbook. Some of the more important and relevant of these are explained below - definitions of the simplest and most general terms will be found in standard undergraduate textbooks.

A few words have acquired specialized meanings in certain areas of chemistry; the particular meanings of such words in the context of solution chemistry are included here.

Aprotic solvent. A solvent which has no readily ionizable protons. Thus dimethyl sulphoxide is classed as an aprotic solvent - and ethanol is only protic with respect to its hydroxyl proton.

Bulk solvent. Strictly this applies to solvent which is unaffected by the presence of solute; but in n.m.r. studies of solvation the word "bulk" is often taken to include anion solvation shells and cation secondary solvation shells (cf. frame 8) when, as is generally the case, they are in rapid equilibrium with bulk solvent.

Hydrodynamic radius. The radius of an ion plus such solvent molecules as move through the solution with it.

Hydrolysis. In inorganic aqueous solution chemistry this term is often applied to the reversible loss of one or more protons from an aquo-cation (cf. frames 33 - 35).

Jahn-Teller distortion. Orbitally degenerate ground states distort themselves so as to remove the degeneracy. The ground states concerned for an octahedral complex are t_{2g}^1, t_{2g}^2, e_g^1, etc. The distortions, and the chemical consequences, are greater for e_g states, as in $Cr^{2+}(t_{2g}^3e_g^1)$ and $Cu^{2+}(t_{2g}^6e_g^3)$, than for t_{2g} examples, e.g. $Ti^{3+}(t_{2g}^1)$. But the Jahn-Teller effect is big enough to affect visible absorption spectra of Ti^{3+}, as seen in frame 22. Consult C S G Phillips and R J P Williams, Inorganic Chemistry, Vol. 2, Oxford (1966), pp. 194,383 for an explanation.

Madelung constant. The coulombic energy of interaction between an ion and its neighbours in a crystal lattice is $-Az_+z_-e^2/4\pi\epsilon_0 r$, where r is the distance between nearest ions, ϵ_0 is the permittivity, e is the charge on the electron, z_+ and z_- are the cation and anion charges, and A is the Madelung constant. A is the sum of a slowly converging series representing the number of neighbours at each of successively increasing interionic distances. A values thus depend on the geometry of the crystal.

pK. $pK = -\log_{10}K$. In this cassette pK values refer specifically to reversible proton loss (hydrolysis - cf. above) from an aquo-cation (cf. frames 33-35).

Polymerization. In aqueous solution chemistry "polymerization" is often used rather imprecisely to cover the formation of oxo- and hydroxo- bridged polynuclear cations (cf. frames 33b, 39). The release of water molecules involved is ignored.

Primary solvation shell. There remains controversy over the precise definition of primary and secondary solvation numbers and shells, especially for those ions where movement of solvent molecules between shells and bulk solvent is very fast. In this Chemistry Cassette the term "primary solvation shell" is used to refer to solvent molecules interacting directly with the ion, while "secondary solvation shell" is used to cover other solvent molecules influenced significantly by the ion.

Protic solvent. A solvent containing ionizable protons (contrast "aprotic solvent" above).

Radial distribution function. If the probability of finding an entity (in this Chemistry Cassette an ion or solvent molecule) in a unit small volume is Ψ^2, then the probability of finding the entity at a distance between r and $r+\delta r$ from a central reference point will be $4\pi r^2\Psi^2\delta r$. This quantity is the product of the probability per unit volume and the volume of space between the spheres of radius r and $r+\delta r$. The radial distribution function, or the probability of the entity being at distance r, is thus $4\pi r^2\Psi^2$.

Secondary solvation shell. See "primary solvation shell" above.

Stability. This should be used only in a thermodynamic sense: "inert" is the correct word for what is loosely called "kinetically stable". It is advisable to specify what aspect of stability is meant in a particular case - stability to air, to oxidation, to water, to light, to polymerization, etc.

Term. In the language of spectroscopy "term" has the specific meaning of an energy level for a system. For a given configuration, for instance the $\underline{d}^n$ configuration of a transition metal ion, there will in general be several "terms", or discrete energy levels. For example, a $\underline{d}^2$ configuration (as in V^{3+}) has terms ^1S, ^3P, ^1D, ^3F and ^1G (see G Herzberg: Atomic Spectra and Atomic Structure, Prentice Hall-Dover, 1944, chap. 3, pp 130 et seq. Chapter 3 of B N Figgis, Introduction to Ligand Fields, Interscience, New York, 1966 is more recent and more angled to transition metal cases, but less simple in approach than Herzberg.)

FURTHER READING

The following bibliography gives suggestions for further reading to obtain a different or fuller view of various topics. "Metal Ions in Solution" by the present author (published by Ellis Horwood ltd., Chichester in 1978, paperback 1979; distributed by John Wiley) covers all the ground of this cassette and of its planned thermodynamic and kinetic successor in greater detail, giving much more information and fuller literature references.*

GENERAL

O Popovych and R P T Tomkins: Non-aqueous Solution Chemistry, Wiley, 1981.

B E Conway: Ionic Hydration in Chemistry and Biophysics, Elsevier, 1981.

These recent books contain a great deal about many facets of the chemistry of ions in solution.

J O'M Bockris and A K N Reddy: Modern Electrochemistry, Plenum-Rosetta, 1973. (Two vols.).

Chapters 2 and 4 of Volume 1 include general descriptions of ion solvation.

J E Desnoyers and C Jolicoeur, in Modern Aspects of Electrochemistry, Vol. 5, ed. B E Conway and J O'M Bockris, Butterworths, 1969, chap. 1, pp16-40.

J I Padova, ibid, Vol. 7, 1972, chap. 1.

These reviews provide a brief overview of several aspects of the solvation of ions in water and in mixed and non-aqueous solvents.

AQUO-METAL IONS

Information on these will be found in most undergraduate textbooks on inorganic chemistry.

D T Richens and A G Sykes: Comments on Inorganic Chemistry, 1 , 141 (1981).

This article describes the chemistry of the aquo-

ions of molybdenum in various oxidation states, and is of interest in relation to the topic of recent and forthcoming characterization of aquo-ions.

ION SOLVATION

J N Murrell and E A Boucher: Properties of Liquids and Solutions, Wiley, 1982

A general description of ion hydration.

P Kebarle, in Modern Aspects of Electrochemistry, Vol 9, ed. B E Conway and J O'M Bockris, Plenum, 1974, pp 1 - 46.

A more advanced and detailed treatment of ion hydration.

S F Lincoln: Coord. Chem. Rev., 6, 309 (1971).
A Fratiello: Progr. Inorg. Chem., 17, 57 (1972).

Reviews of the determination of solvation numbers by n.m.r. techniques.

R K Harris and B E Mann (eds.): NMR and the Periodic Table, Academic Press, 1978.

This book gives a good indication of the versatility of n.m.r. as a means of probing ion solvation, especially by the use of n.m.r. signals from elements scattered throughout the periodic table.

A I Popov: Pure App. Chem., 41, 275 (1975).

A short conference lecture demonstrating how n.m.r. and infrared-Raman spectroscopies give complementary information on ion solvation.

D E Irish, in Ionic Interactions, Vol. 2, ed. S Petrucci, Academic Press, 1971, chap. 9.
R E Verrall, in Water - A Comprehensive Treatise, Vol. 3, ed. F Franks, Plenum, 1973, ch. 5.

These chapters detail how vibrational spectroscopy furnishes information on solvated ions.

B N Figgis: Introduction to Ligand Fields, Wiley, 1966.

Chapters 3, 4, 7 and 9 detail ultraviolet-visible spectra of hydrated transition metal cations and explain how ligand field parameters are obtained.

G Herzberg: Atomic Spectra and Atomic Structure, Prentice Hall-Dover, 1944.
W G Richards and P R Scott: Structure and Spectra of Atoms, Wiley, 1976, chaps. 3 and 4.

These books are recommended to readers whose knowledge of atomic spectroscopy is insufficient to cope with the basics used by Figgis.

D Feakins, R O'Neill and E Waghorne: Pure App. Chem., 54, 2317 (1982).

A short account of an important recent development in obtaining single ion hydration numbers from ion movement experiments.

SOLVATION NUMBERS

J F Hinton and E S Amis: Chem. Rev., 71, 627 (1971).

Probably the most exhaustive compilation of hydration and solvation numbers. Fairly uncritical (which is unfortunate but very understandable in the light of the enormous amount of data).

ION-SOLVENT DISTANCES

J E Enderby and G W Neilson, in Water - A Comprehensive Treatise, Vol. 6, ed. F Franks, Plenum, 1979, chap. 1.
R Caminiti, G Licheri, G Piccaluga and M Magini, Rev. Inorg. Chem., 1, 333 (1979).

Thorough descriptions and reviews of the estimation of ion-solvent distances by X-ray and neutron diffraction studies of concentrated aqueous salt solutions.

H Ohtaki: X-ray Diffraction Studies on the Structures of Metal Complexes in Solution, Rev. Inorg. Chem., 4, 103, (1982).

A most detailed and up-to-date account of ion-solvent distances as determined by X-ray techniques.

The book by Murrell and Boucher cited at the start of the Ion Solvation section of this list includes a useful short account of the application of diffraction techniques to ionic solutions.

HYDROLYSIS AND POLYMERIZATION

C F Baes and R E Mesmer: The Hydrolysis of Cations, Wiley, 1976.

The definitive book on this area - thorough and comprehensible.

F R Hartley, C Burgess and R Alcock: Solution Equilibria, Ellis Horwood, Chichester, 1980.

Although dealing primarily with complexes this book gives a good idea of how to design experiments and compute results. The methods and approach are very relevant to hydrolysis and polymerization equilibria in aqueous solution.

* At the time of preparing this cassette (July 1983) there are plans to publish (Ellis Horwood) an undergraduate text "Inorganic Solution Chemistry" which will deal with the chemistry of ions in solution at a level similar to that of this Chemistry Cassette.

An essential guide for all teachers of chemical kinetics...

REACTION KINETICS: a Resource for Teachers

by **B E Dawson,** King's College, London
C L Mason, Strode's College, Egham
P Mason, Wimbledon High School

This is not a conventional textbook but rather a commentary on current thought and practice in reaction kinetics. It contains two distinct sections; a survey of educational ideas, and a survey of school based studies and resources.

It begins with a review of potential objectives for a course in chemical kinetics, allocating these to three stages of development; introductory, intermediate and undergraduate. It then provides an account of different methods of collection, presentation and interpretation of kinetic data, and offers a selection of studies using data from the literature. A survey of school based studies and resources is also included.

The book was written by chemists actively concerned in the teaching of kinetics, both at tertiary and secondary levels, at the instigation of the Educational Techniques Group of the Royal Society of Chemistry.

Price: £3.50 (£2.50 to members of the Royal Society of Chemistry).
Post & packing: 50p.

Available from the Secretary of the Education Division,
The Royal Society of Chemistry, Burlington House, London W1V 0BN.