

Contents

GLOSSARY OF NOTATION	xi
1. THE WATER MOLECULE	1
1.1. The water molecule: description based on experiment	1
(a) Composition	1
(b) Energetics of formation	2
(c) Molecular dimensions	4
(d) Molecular vibrations	6
(e) Electrical properties	12
(f) Comparison of molecular energies	17
1.2. The water molecule: description based on theory	21
(a) Electrostatic models	21
(b) Molecular orbital theory	23
(c) Electron density distribution	27
(d) Accurate wave functions and the calculation of physical properties	31
(e) The charge distribution: a summary	34
2. THE REAL VAPOUR	36
2.1. Forces between water molecules	36
(a) Origin and description of the forces	36
(b) Virial coefficients	48
(c) Forces between water molecules: a summary	56
2.2. Thermodynamic properties	58
(a) Pressure–volume–temperature relations	58
(b) Thermal energy	65
3. ICE	71
3.1. Structure of ice I	71
(a) Positions of the oxygen atoms	71
(b) Positions of the hydrogen atoms	74
(c) Amplitudes of thermal vibration	77
(d) Structure of ice I: a summary	77
3.2. Structures of ice polymorphs	79
(a) Ices II, III, and V	79
(b) Ices VI, VII, and VIII	87
(c) Vitreous ice and ice Ic	89
(d) Structural characteristics of ice polymorphs: a summary	91

3.3. Thermodynamic properties	92
(a) Phase relations	92
(b) Thermal energy	98
(c) P - V - T data for ice I	102
3.4. Electrical properties and self-diffusion	105
(a) Dielectric constant and dipole moment	105
(b) Dielectric polarization and relaxation	112
(c) Electrical conductivity	118
(d) Self-diffusion	120
3.5. Spectroscopic properties	121
(a) Vibrational spectrum of ice I	121
(b) Vibrational spectra of ice polymorphs	132
(c) Nuclear magnetic resonance	135
3.6. Hydrogen bonding	137
(a) Experimental energy of hydrogen bonding	137
(b) Potential functions for hydrogen-bonded molecules	141
(c) Theoretical description of the hydrogen bond in ice	143
(d) The properties of ice as determined by hydrogen bonds: a summary	148
4. PROPERTIES OF LIQUID WATER	150
4.1. Introduction	150
(a) Meaning of the term 'structure' as applied to liquid water	150
(b) Liquid structure and experimental techniques	154
4.2. X-ray diffraction	155
(a) Radial distribution functions	155
(b) Interpretation of the radial distribution function in terms of V-structures	163
4.3. Thermodynamic properties	171
(a) Thermal energy	172
(b) Pressure-volume-temperature relations	182
4.4. Static dielectric constant and NMR chemical shift	189
(a) Static dielectric constant	189
(b) NMR chemical shift	194
4.5. Optical properties	197
(a) Refractive index	197
(b) Light scattering	200
4.6. Properties depending on the rates of molecular displacements	205
(a) Dielectric relaxation	206
(b) Relaxation of nuclear magnetism	214
(c) Self-diffusion	217
(d) Viscosity	222
(e) Ionic dissociation and migration	224
(f) Molecular displacements: a summary	227

CONTENTS

ix

4.7. Vibrational spectroscopy	228
(a) Identification of spectral bands	229
(b) The O-H and O-D stretching bands	231
(c) Intermolecular vibrations	242
(d) Overtone and combination bands	245
4.8. The structure of water: conclusions based on properties	246
(a) Problems of describing the properties of water in terms of hydrogen bonds	246
(b) The V-structure of water: a summary	250
(c) The D-structure of water: a summary	251
5. MODELS FOR LIQUID WATER	254
5.1. Small-aggregate models	255
5.2. Mixture and interstitial models	256
(a) Basic premiss	256
(b) Details of several models	257
(c) Consistency of mixture models with experimental data	264
5.3. Distorted hydrogen-bond models	265
ADDENDUM	268
BIBLIOGRAPHY	271
AUTHOR INDEX	283
SUBJECT INDEX	289

Boltzmann's constant, k . Various force constants
 E (erg) = 10^7 dyn cm⁻²
 Molecular dipole moment in a condensed phase
 Avogadro's number
 Number of molecules per unit volume
 Refractive index
 Pressure
 Quadrupole moment
 Gas constant
 Entropy
 Temperature, in °K unless stated otherwise
 Temperature in °C. Time
 Potential energy
 Molar volume
 Fractional quantum number
 Electrostatic potential
 Mole fraction of component A
 Molecular polarizability
 Coefficient of cubical expansion
 Coefficient of adiabatic compressibility
 Coefficient of isothermal compressibility