

WATER

A COMPREHENSIVE TREATISE



Volume 1
The Physics and
Physical Chemistry
of Water

Edited by Felix Franks

WATER

A COMPREHENSIVE TREATISE

Edited by Felix Franks

*Unilever Research Laboratory
Sharnbrook, Bedford, England*

Volume 1

The Physics and Physical Chemistry of Water

 **PLENUM PRESS • NEW YORK—LONDON • 1972**

Library of Congress Catalog Card Number 78-165694
ISBN 0-306-37181-2

© 1972 Plenum Press, New York
A Division of Plenum Publishing Corporation
227 West 17th Street, New York, N.Y. 10011

United Kingdom edition published by Plenum Press, London
A Division of Plenum Publishing Company, Ltd.
Davis House (4th Floor), 8 Scrubs Lane, Harlesden, London, NW10 6SE, England

All rights reserved

No part of this publication may be reproduced in any
form without written permission from the publisher

Printed in the United States of America

WATER
A COMPREHENSIVE TREATISE
Volume 1
The Physics and
Physical Chemistry of Water

αριστον μεν ὕδωρ.

PINDAR

Preface

Although the Greek philosophers and poets were acutely aware that water plays a very special role in Nature, the attitude among modern scientists has been along the lines of “familiarity breeds contempt.” With a very few notable exceptions, the scientific community has taken this liquid very much for granted, and active interest on a significant scale only dates from the early 1960’s. Since then progress has been slow, but it has been finite. However, for a triatomic molecule water has presented physicists, chemists, biologists, and technologists with a large number of practical and conceptual problems. The renewed interest in their solution during the past decade has been greatly assisted by the active support of the U. S. Office of Saline Water, but even acknowledging all that has been achieved, we have barely scratched the surface. Perhaps the most significant achievement is that we are now beginning to understand the nature of the problem confronting us.

It is against this background that this volume should be approached, at a time when even simple liquids still present us with many unsolved mysteries. In the various chapters of this book a range of properties of water is discussed and it is in the nature of the general problem that conclusions based on the application of any one experimental technique cannot always be easily reconciled with results derived from the use of another technique. Indeed, some of the interpretations advanced for observed phenomena are by no means universally accepted by the scientific “water community”—this became very evident during the first Gordon Research Conference on Water and Aqueous Systems, held in 1970.

The aims in publishing this volume at this particular time are threefold: to review the physical and theoretical techniques which have been and are being applied to a study of the intermolecular nature of water; to discuss critically the type of information obtainable by these techniques, hopefully

to arrive at some temporary consensus model or models; and to present reliable physical data pertaining to water under a range of conditions, i.e., "Dorsey revisited," albeit on a less ambitious scale.

I should like to acknowledge a debt of gratitude to several of my colleagues, to Prof. D. J. G. Ives and Prof. Robert L. Kay for valuable guidance and active encouragement, to the contributors to this volume for their willing cooperation, and to my wife and daughters for the understanding shown to a husband and father who hid in his study for many an evening. My very special thanks go to Mrs. Joyce Johnson, who did all the correspondence and much of the arduous editorial work with her usual cheerful efficiency.

F. FRANKS

Biophysics Division

Unilever Research Laboratory Colworth/Welwyn

Colworth House, Sharnbrook, Bedford

March 1972

Contents

Chapter 1

Introduction—Water, the Unique Chemical

F. Franks

1.	Introduction	1
2.	The Occurrence and Distribution of Water on the Earth	2
3.	Water and Life	4
4.	The Scientific Study of Water—A Short History	8
5.	The Place of Water among Liquids	13

Chapter 2

The Water Molecule

C. W. Kern and M. Karplus

1.	Introduction	21
2.	Principles of Structure and Spectra: The Born–Oppenheimer Separation	22
3.	The Electronic Motion	26
3.1.	The Ground Electronic State of Water	31
3.2.	The Excited Electronic States of Water	50
4.	The Nuclear Motion	52
5.	External-Field Effects	70
5.1.	Perturbed Hartree–Fock Method	74
5.2.	Perturbed Configuration Interaction Method	78
6.	Conclusion	80

Appendix A. Bibliography of Theoretical Calculations on the Electronic Structure of the Water Molecule (1925–1970)	80
Appendix B. Definition of the Symbols Appearing in T_N	88
Appendix C. Definition of the Symbols Appearing in E_{vib} and $\mathcal{H}_{\text{rot}}^v$	89
Appendix D. Definition of the Symbols Appearing in the Rotational Matrix Elements	90

*Chapter 3***Theory of Hydrogen Bonding in Water**

C. N. R. Rao

1. Introduction	93
2. Early Theoretical Studies of the Hydrogen Bond	94
3. Potential Function for the Hydrogen Bond	96
4. Recent Theoretical Methods	98
5. Water Dimer	99
6. Water Polymers	104
7. Spectroscopic Properties, Proton Potential Functions, Charge Distribution, and Related Aspects	107
8. Conclusions	113

*Chapter 4***The Properties of Ice**

F. Franks

1. Introduction	115
2. Phase Behavior of Ice	116
3. Structures of Crystalline Ice Phases	118
4. Thermodynamic Properties of Ice Polymorphs	123
5. Mechanical Properties	129
6. Lattice Dynamics	131
7. Molecular and Ionic Transport in Ice	136
7.1. Dielectric Properties	136
7.2. Self-Diffusion	140
7.3. Electrical Conductivity	141
7.4. Orientational and Ionic Defects in Ice; Theories of Transport Mechanisms	144
8. Summary	148

*Chapter 5***Raman and Infrared Spectral Investigations of Water Structure**

G. E. Walrafen

1.	Introduction	151
2.	New Experimental Techniques	153
2.1.	Stimulated Raman Scattering	153
2.2.	Hyper-Raman or Inelastic Harmonic Light Scattering	154
2.3.	Fixed-Beam Laser-Raman Method	155
3.	Intermolecular Vibrations of H ₂ O and D ₂ O	158
3.1.	The Restricted Translational Region	158
3.2.	The Librational Region	165
3.3.	The Five-Molecule, Fully Hydrogen-Bonded C _{2V} Structural Model	170
4.	Intramolecular Vibrational Spectra from HDO in H ₂ O and D ₂ O	174
4.1.	Raman Spectra	174
4.2.	Infrared Absorbance Spectra	189
4.3.	Stimulated Raman Spectra	193
4.4.	Near-Infrared Spectra	195
5.	Intramolecular Vibrational Spectra from H ₂ O and D ₂ O ..	197
5.1.	Spontaneous and Stimulated Raman Spectra	197
5.2.	Infrared Spectra	201
6.	Relation of Component Properties to Water Structure ..	203
7.	Thermodynamic Tests of the Consecutive Hydrogen-Bond Disruption Model	205
8.	Current and Future Work	214

*Chapter 6***Nuclear Magnetic Resonance Studies on Water and Ice**

Jay A. Glasel

1.	Theoretical and Experimental Foundations of Magnetic Resonance	215
1.1.	Properties of Nuclei in Electric and Magnetic Fields	216
1.2.	Spectroscopic Parameters Describing Nuclear Magnetic Resonance	218
1.3.	Experimental Arrangements	222
2.	Magnetic Shift and Spin Coupling Phenomena in Water Vapor, Water, and Ice	223

2.1.	Theory of Chemical Shift	223
2.2.	Measurement of Deuteron and ^{17}O Chemical Shifts in Water	229
2.3.	Structural Interpretations of Chemical Shift Measurements	230
2.4.	Measurements of Spin-Spin Coupling Constants ...	233
3.	Measurement and Interpretation of Magnetic Relaxation Times in Water and Ice.....	233
3.1.	Dipole-Induced Relaxation.....	234
3.2.	Measurement and Interpretation of Proton Relaxation in Water.....	235
3.3.	Measurement and Interpretation of Proton Relaxation in Ice	241
3.4.	Quadrupole-Induced Relaxation	244
3.5.	Measurement and Interpretation of Deuteron and ^{17}O Relaxation in Water	245
3.6.	Summary of Relaxation Experiments on Liquid Water	249
3.7.	Measurement of Self-Diffusion Coefficient	249
3.8.	Measurement of Kinetic Rate Constants in Water .	250
4.	The Contributions of NMR Methods to the Structure Problem in Liquid Water	252
4.1.	Results from Chemical Shift Measurements	252
4.2.	Results from Relaxation Measurements	253

*Chapter 7***Liquid Water: Dielectric Properties**

J. B. Hasted

1.	Introduction	255
2.	The Electrical Properties of the Free Water Molecule ...	256
3.	The Measured Static Dielectric Constant.....	260
4.	Theory of the Static Dielectric Constant	263
5.	The Static Dielectric Constant Calculated on Various Models	267
6.	Interpretation of Static Dielectric Constant with Induced-Dipole Contribution	275
7.	Microwave and Submillimeter Dielectric Constants	276
8.	Kinks?	289
9.	Submillimeter Measurements	291
10.	Theory of the Dielectric Constant in a Time-Varying Field	295

11.	Interpretation of the Relaxation Times and Absorption Bands	300
12.	Interpretation of Data in the Submillimeter Band. Conclusions	305

*Chapter 8***Liquid Water: Scattering of X-Rays**

A. H. Narten and H. A. Levy

1.	Introduction	311
2.	Experimental Methods	311
2.1.	Large-Angle Scattering	312
2.2.	Small-Angle Scattering	315
2.3.	Data Reduction	316
3.	Analysis of Diffraction Data	317
3.1.	Scattering by Heteroatomic Liquids	317
3.2.	Scattering by Model Liquids	321
4.	Diffraction Pattern of Liquid Water	322
4.1.	Survey of Experimental Data	324
4.2.	Interpretation of the Diffraction Pattern	324
5.	Conclusions	331

*Chapter 9***The Scattering of Neutrons by Liquid Water**

D. I. Page

1.	Introduction	333
2.	The Neutron Scattering Method	334
2.1.	Nuclear Scattering of Neutrons	334
2.2.	Coherent and Incoherent Scattering	335
2.3.	Isotopic Substitution	337
2.4.	The Scattering Law and Correlation Functions	339
2.5.	Neutron Spectra from Water	342
3.	Structural Measurements	344
3.1.	Structure Factor for Water	344
3.2.	Molecular Structure Factors	346
4.	Quasielastic Scattering of Neutrons by Water	349
4.1.	Debye–Waller Factor	349
4.2.	Diffusive Motions	350

5.	Inelastic Scattering of Neutrons by Water	354
5.1.	Spectral Density Function	354
5.2.	Experimental Results	355
6.	Discussion	359
	Appendix. Calculation of Orientational Correlation Factors for Molecules	361

*Chapter 10***Thermodynamic and Transport Properties of Fluid Water**

G. S. Kell

1.	Introduction	363
2.	Thermodynamic Properties	365
2.1.	The Macroscopic Viewpoint	365
2.2.	Volume Properties	366
2.3.	Thermal Properties	385
2.4.	Liquid-Vapor Equilibria	391
2.5.	Critical Point	394
3.	Transport Properties	399
3.1.	The Hydrodynamic Viewpoint	399
3.2.	Vapor	401
3.3.	Liquid	404

*Chapter 11***Application of Statistical Mechanics in the Study of Liquid Water**

A. Ben-Naim

1.	Introduction	413
2.	Characteristic Features of an Effective Pair Potential for Liquid Water	420
3.	Application of the Percus-Yevick Equation	426
4.	Application of the Monte Carlo Technique	430
5.	Some Specific Applications of the Pair Correlation Function	433
5.1.	Density Fluctuations in Water	433
5.2.	Local Structure Index for Water	436
5.3.	Hole and Particle Distributions in Water	439
5.4.	A Possible Exact Definition of the Structure of Water	440

*Chapter 12***Liquid Water—Acoustic Properties: Absorption and Relaxation**

Charles M. Davis, Jr., and Jacek Jarzynski

1.	Introduction	443
2.	Ultrasonic Absorption	444
3.	Ultrasonic Techniques	447
	3.1. Acoustic System	447
	3.2. Pressure- and Temperature-Control Systems	448
	3.3. Electronics	449
4.	Experimental Results	450
	4.1. Volume Viscosity	454
5.	Relaxational Compressibility	457
6.	Structural Relaxation Time	458
7.	Conclusions	461

*Chapter 13***Water at High Temperatures and Pressures**

Klaus Tödheide

1.	Introduction	463
2.	Thermodynamic Properties.....	464
	2.1. PVT Data and Equation of State	465
	2.2. Thermodynamic Functions	474
3.	Transport Properties	482
	3.1. Viscosity	483
	3.2. Self-Diffusion.....	487
	3.3. Thermal Conductivity	488
4.	Electrical Properties	490
	4.1. Static Dielectric Constant	490
	4.2. Specific Conductance and Ionic Conductances	495
5.	Ionic Product	502
6.	Spectroscopic Studies	504
	6.1. Infrared Spectral Studies	505
	6.2. Raman Spectral Studies	507
	6.3. Interpretation of Spectroscopic Results with Respect to Water Structure	510
7.	Concluding Remarks	513

*Chapter 14***Structural Models**

Henry S. Frank

1.	The Nature of Models	515
2.	Requirements a Water Model Must Attempt to Satisfy... .	516
3.	Some Properties of Water of Special Current Interest ...	518
3.1.	Thermodynamic and Mechanical Properties; Structure and Fluctuations	518
3.2.	X-Ray Scattering; Structure and Fluctuations	519
3.3.	Hydrogen Bonds and Structure	520
3.4.	Spectroscopic Properties: Broken Hydrogen Bonds .	522
3.5.	Vapor-Pressure Isotope Effect	525
3.6.	Molecular Motions	527
4.	Brief Survey of Models	530
4.1.	Mixture Models	532
4.2.	Uniformist Models.....	534
4.3.	Interstitial Models	535
5.	The Present “Best Guess”	536
5.1.	Bonding	537
5.2.	Structure Pattern	537
5.3.	Equilibrium Relations	540
5.4.	Molecular Motions	541
5.5.	Heat Capacity	542
	References	545
	Index	579

Contents of Volume 2: Water in Crystalline Hydrates; Aqueous Solutions of Simple Nonelectrolytes

- Chapter 1.* The Solvent Properties of Water, by F. Franks
- Chapter 2.* Water in Stoichiometric Hydrates, by M. Falk and O. Knop
- Chapter 3.* Clathrate Hydrates, by D. W. Davidson
- Chapter 4.* Infrared Studies of Hydrogen Bonding in Pure Liquids and Solutions, by W. A. P. Luck
- Chapter 5.* Thermodynamic Properties, by F. Franks and D. S. Reid
- Chapter 6.* Phase Behavior of Aqueous Solutions at High Pressures, by G. M. Schneider
- Chapter 7.* Dielectric Properties, by J. B. Hasted
- Chapter 8.* Spectroscopic Properties, by M. J. Blandamer and M. F. Fox
- Chapter 9.* Acoustic Properties, by M. J. Blandamer
- Chapter 10.* NMR Spectroscopic Studies, by M. D. Zeidler
- Chapter 11.* Molecular Theories and Models of Water and of Dilute Aqueous Solutions, by A. Ben-Naim

Contents of Volume 3: Aqueous Solutions of Simple Electrolytes

- Chapter 1.* Thermodynamics of Ion Hydration, by H. Friedman and C. V. Krishnan
- Chapter 2.* Thermodynamics of Mixed Electrolytes, by R. H. Wood and H. Anderson
- Chapter 3.* Hydration Effects in Acid-Base Equilibria, by L. Hepler and E. M. Woolley
- Chapter 4.* Ion Transport in Water and Mixed Aqueous Solvents, by R. L. Kay
- Chapter 5.* Infrared Spectroscopy, by R. E. Verrall
- Chapter 6.* Raman Spectroscopy, by T. H. Lilley
- Chapter 7.* NMR Relaxation Spectroscopy, by H. G. Hertz
- Chapter 8.* Dielectric Properties, by R. Pottel

Contents of Volume 4: Aqueous Solutions of Macromolecules; Disperse Systems

Hydration and Aggregation in Aqueous Solutions of Solutions of Small Solutes

Chapter 1. Surfactants, by G. C. Kresheck

Chapter 2. Dyestuffs, by C. H. Giles and D. G. Duff

Chapter 3. Lipids, by H. Hauser

The Role of Solute-Water Interactions in Aqueous Solutions and Gels of Macromolecules

Chapter 4. Nucleic Acids, Peptides, and Proteins, by D. Eagland

Chapter 5. Polysaccharides, by A. Suggett

Chapter 6. Synthetic Polymers, by P. Molyneux

Disperse Systems

Chapter 7. Role of Water in the Stability of Hydrophobic Colloids, by D. Eagland

Chapter 8. Adsorption of Water on Well-Characterized Solid Surfaces, by A. C. Zettlemoyer

Chapter 9. Clay-Water Systems, by E. Forslind