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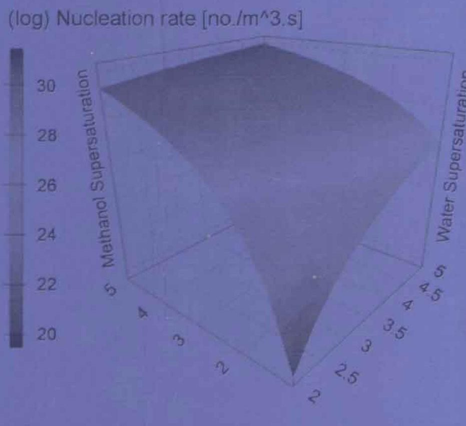
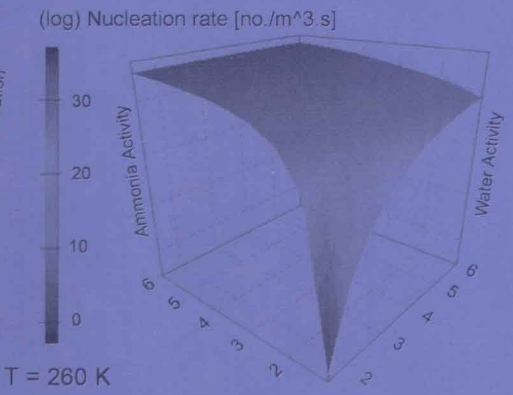
AQUEOUS SYSTEMS AT ELEVATED TEMPERATURES AND PRESSURES

Physical Chemistry in Water, Steam and Hydrothermal Solutions





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Physical Chemistry in Water, Steam and Hydrothermal Solutions

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IAPWS

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The International Association for the Properties of Water and Steam

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AQUEOUS SYSTEMS AT ELEVATED TEMPERATURES AND PRESSURES

Physical Chemistry in Water, Steam and Hydrothermal Solutions

Preface

The International Association for the Properties of Water and Steam (IAPWS) has produced this book in order to provide an accessible, up-to-date overview of important aspects of the physical chemistry of aqueous systems at high temperatures and pressures. These systems are central to many areas of scientific study and industrial application, including electric power generation, industrial steam systems, hydrothermal processing of materials, geochemistry, and environmental applications. Our goal is to present the material at a level that serves both the graduate student seeking to learn the state of the art, and also the industrial engineer or chemist seeking to develop additional expertise or to find the data needed to solve a specific problem.

The wide range of people for whom this topic is important should represent a sizable audience for this book, but it also provides a challenge. Advanced work in this area is distributed among physical chemists, chemical engineers, geochemists, and other specialists, who may not be aware of parallel work by those outside their own specialty. The particular aspects of high-temperature aqueous physical chemistry of interest to one industry may be irrelevant to another; yet another industry might need the same basic information but in a very different form.

To serve all these constituencies, we solicited several chapters that cover the foundational thermophysical properties (such as gas solubility, phase behavior, thermodynamic properties of solutes, and transport properties) that are of interest across numerous applications. The presentation of these topics is intended to be accessible to readers from a variety of backgrounds. Other chapters address fundamental areas of more specialized interest, such as critical phenomena and molecular-level solution structure. Several chapters are more application-oriented, addressing areas such as power-cycle chemistry and hydrothermal synthesis. As befits the variety of interests addressed, some chapters provide more theoretical guidance while others, such as those on acid/base equilibria and the solubilities of metal oxides and hydroxides, emphasize experimental techniques and data analysis.

We expect that some readers of this book will find some chapters that are not of interest; therefore, we do not discourage selective reading, especially for those in industry whose interests may be dictated by specific practical problems. To this end, each chapter is meant to stand on its own with cross-referencing to other chapters should the reader require more detailed clarification. This treatise is not intended to provide an exhaustive review of recent research in each field, although references are generally provided to allow the interested reader to delve deeper into each topic. However, the thermodynamic principles and data selection criteria outlined in these chapters should provide a firm basis for design and operation in many industrial and geochemical applications, as well as for scientific modeling.

Authors were encouraged to provide tables of data and correlation parameters (or references to reliable sources of data) and sample calculations where appropriate, so that readers will have the tools to perform calculations for the systems of interest to them.

This book is a product of the International Association for the Properties of Water and Steam (see www.iapws.org). While IAPWS has historically been known primarily for producing the international standards for water properties embodied in "steam tables" (see Chapter 1), its expertise has expanded into other aspects of high-temperature aqueous systems, as reflected in its Working Groups on Power Cycle Chemistry and the Physical Chemistry of Aqueous Solutions. These groups use the latest science to produce recommendations for industrial and scientific practice in many areas of high-temperature aqueous physical chemistry. A major motivation for producing this book was to disseminate the expert knowledge of the IAPWS community to a wider audience.

As Editors, we owe special thanks to many people. The assistance and advice of Dr. R. Barry Dooley, the Executive Secretary of IAPWS, were invaluable during the planning stages of the process. Professor Peter Tremaine played an important role in the early organization of the book. Pacific Publications, Inc. was employed to standardize the format of the chapters and prepare them for submission to the publisher. We would also like to thank all of the contributing authors for their patience and understanding during the rounds of internal editing, and for their combined conviction to produce a readily readable book while maintaining the highest scientific standards.

Last but not least, we express our gratitude to Prof. Dr. Ulrich Franck, whose original idea for an "Atlas on Hydrothermal Chemistry" provided us with the initial impetus to produce a volume of useful information on high-temperature aqueous systems. Professor Franck has been a leader in many of the areas of research covered in this book, and we are honored that he volunteered to write a Foreword for us.

Donald A. Palmer,
Roberto Fernández-Prini, and
Allan H. Harvey

Oak Ridge, Buenos Aires, and Boulder, November 2003

Foreword

This book shall serve a triple purpose. It is hoped that it will provide engineers and scientists with an understanding of the latest methods and approaches taken in each area, including examples of application of the latest treatments and critically selected, condensed and easily accessible data. The information shall also be useful as a basis for further theoretical understanding and development by specialist and non-specialist alike. The material given should create new prospects for future experimental research and engineering processes. The traditional industrial users of this knowledge have been in the steam power industry; however, at present it must also serve other fields like hydrothermal processes, waste treatment, the oil industry, and many applications in the geosciences.

By the first decade of the twentieth century, the thermodynamic basis for the operation of steam turbines to produce electricity was well understood. Manufacturers of boilers and turbines calculated the capacity and efficiency of their products, while purchasers of their equipment used similar calculations to write specifications for performance. Such calculations depend on accurate values of the thermodynamic properties of water and steam. The existence of several conflicting sets of tables for these properties posed a major problem. Thus, in 1929, the first International Steam Table Conference was held in London with the objective of preparing an internationally accepted set of tables. Six similar conferences were held through 1964 in order to make improvements in a systematic manner. Expanded coverage was also needed because of advances in power-plant technology that required boilers and turbines to operate at higher temperatures and pressures. The earlier results were so-called skeleton tables: uniform grids of data points. It had been recognized from the start that representation by equations would be desirable. The development of computers enhanced the capabilities to devise equations that would fit comprehensive sets of accurate data. An "International Formulation Committee", IFC, designed a formulation for scientific and general use and a separate "industrial" formulation for the needs of the steam power industry. Many books of steam tables were published based on these formulations.

By 1968, it became evident that a stable organizational structure was needed and the International Association for the Properties of Steam (IAPS, which in 1989 added "Water" to its name and became IAPWS) was established. International conferences were subsequently held every five years. The need for precise thermodynamic data for wider varieties of scientific calculations and technical investigations of various aqueous systems led to improved formulations for general and scientific use, most recently the "IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use." Shortly afterwards, IAPWS approved a new Industrial Formulation for the Properties of Water and Steam (IF97), which provided industrial users with a fast, state-of-the-art tool for calculation of turbine efficiencies.

There is increasing need for data for other properties of water, steam, and aqueous systems. The viscosity is relatively easy to measure and is available from experiments to supercritical temperatures and 300 MPa. This is true to some extent for thermal conductivity, which is less widely investigated. Knowledge of diffusion coefficients in dense supercritical aqueous phases is very scarce, although of considerable value for discussions of the kinetics of chemical reactions in such fluids. Estimates based on water viscosity and molecular sizes can be helpful. Of particular interest is the static dielectric constant, which even at supercritical temperatures and liquid-like density allows dissociation of dissolved electrolytes. Closely related to the dielectric constant is the ion product of pure water, which is difficult to determine even at moderate temperatures and densities. Because of its positive temperature coefficient, the ion product of water can reach very high values at high density. Static conductivity measurements indicate that at 1000 °C and 10 GPa, water is 1% ionized, while shock-wave measurements at this temperature and a density of 2 g/cm^3 suggest complete ionization, which means that the dense 1000 °C water resembles a fused salt. It has been suggested that such "ionic water" may be a component of the outer planets.

The ability of dense high-temperature or supercritical water to act as a good solvent for ions leads to a number of special phenomena and applications. Some of these can make use of the combination of high solubility and high fluidity, *i.e.*, of high diffusion and convection velocities. Crystal growth, including the hydrothermal growth of perfect single-crystal quartz from supercritical aqueous silica solutions, has been performed. A number of other hydrothermal crystal syntheses are possible. A promising possibility is supercritical electrolytic decomposition, which can be performed with rather concentrated solutions with very high current density and diminishing over-voltage. It is obvious that the understanding of hydrothermal and dense supercritical solutions is particularly relevant to mineralogy and petrology, became many mineral deposits have been formed or changed in hydrothermal phases.

Dense supercritical water has properties that let it almost appear as a special fourth state of aggregation with continuous variation between a highly polar liquid and a gaseous nonpolar fluid. Wide ranges of temperature exist where, even at liquid-like densities, nonpolar gases are completely miscible with supercritical water. This has been observed for the rare gases, for hydrogen, for the atmospheric gases and for the very important combination of carbon dioxide and water. Not only methane and the other smaller alkanes mix with water, but the miscibility of benzene has been observed and quantitatively measured. There is good evidence that such hydrothermal miscibility exists for other, larger organic molecules and one can have regions where "oil and water mix." Efforts have been made to determine phase diagrams and critical curves by computer simulations, which also provide knowledge of intermolecular interactions.

A number of technical applications are already in operation or can be foreseen. One of these is the enhanced recovery of oil from difficult natural deposits. Other types of extraction can be expected, particularly with extracting fluids containing polar and nonpolar components. Supercritical aqueous fluids can also serve as media for chemical reactions, for example for hydrogenation with small residence times in the aqueous reaction area. Supercritical waste disposal is considered, as well as production of fine solid particles from sudden expansion of the fluid solution.

Some phenomena have received special attention because of new experimental results or theoretical advances. These include near-critical phase behavior and the possibility of microemulsions in gas/water systems at very high pressure. The phase behavior of high-pressure ternary water-gas-salt systems could be extensively studied and improved equations of state developed. Combustion and flames in water to supercritical temperatures and pressures of 200 MPa or more seem to be possible and are worth studying.

High-temperature aqueous physical chemistry is fertile ground for scientific and engineering advances; it is hoped that the present volume will stimulate discussions and further developments on these important topics.

Prof. E.U. Franck
Universität Karlsruhe

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Aqueous Systems at Elevated Temperatures and Pressures:
Physical Chemistry in Water, Steam and Hydrothermal Solutions
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Chapter 1

Physical properties of water[☆]

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1.1. Introduction

Water is probably the most familiar chemical compound in human experience, and also the most necessary. We encounter water as clouds, rain, snow, ice, rivers, lakes, and oceans. All known life depends on biochemistry that takes place in aqueous solution; our own bodies consist largely of solutions of various chemicals in water. Sciences as diverse as biochemistry, meteorology, and geology require knowledge of properties of water and aqueous solutions. In the high-temperature aqueous physical chemistry of interest in this book, water is always present in the background as a medium, and sometimes takes a more active role.

In industry, water is an important part of many processes, and understanding of its properties is often necessary for design and optimization, particularly in fluids-based industries such as chemical processing. The industry in which water's thermodynamic properties have been most important is the steam power generation industry. Because of the large quantities of energy (and therefore, money) involved, the power industry needs properties that are not only accurate but also standardized, so that all parties worldwide can have a uniform basis for design, operation, and contracting. The need for standards for water and steam properties in the power industry was the main driving force behind the conferences that ultimately evolved into the International Association for the Properties of Water and Steam (IAPWS), the organization producing this book.

The purpose of this chapter is twofold. First, we want readers to obtain a qualitative understanding of the thermophysical properties of water, particularly the way those properties behave at higher temperatures. Second, we want to tell

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readers how to obtain the most accurate values (for the most part, from standards adopted by IAPWS) for the properties of pure water, both for direct use and for use in the descriptions of aqueous physical chemistry presented in subsequent chapters. We will give equations for some property formulations that are not too complex, but for others we will instead give references where the formulations may be obtained.

1.2. Water at the Molecular Level

1.2.1. Structure of the Water Molecule

Figure 1.1 is a schematic diagram of a single water molecule. The angle at the oxygen atom is approximately 104.5° (close to the 109.5° characterizing a tetrahedral lattice), and the distance from the center of the oxygen atom to the center of each hydrogen atom is approximately 0.096 nm. This geometry varies slightly, depending on the rotational and vibrational state of the molecule and on its surroundings. The values given here are for an isolated molecule in the ground state; even in this case, the geometry is not precisely fixed because of the molecule's zero-point vibrations.

Because the oxygen atom is strongly electronegative, the electron density is enhanced in its vicinity, giving it a partial negative charge that is compensated by a partial positive charge for the hydrogen atoms. As a result, the water molecule has a dipole moment. The most precise measurement of the dipole moment in the ground state (Shostak *et al.*, 1991) is $6.1875(3) \times 10^{-30}$ C·m, where the number in parentheses represents the uncertainty in the last digit. In the units in which dipole moments are typically reported, this is 1.85498(9) debye.

Another molecular property of interest is the dipole polarizability. The polarizability is actually a tensor, but for water the anisotropy is small enough that the mean polarizability (one-third the trace of the tensor) is sufficient for most purposes. The polarizability also depends on frequency; both the zero-frequency (static) limit and the high-frequency (electronic) value are of interest. The static limit includes not only the response of the electrons to an applied electric field, but also a vibrational contribution from the response of the atoms in the molecule.

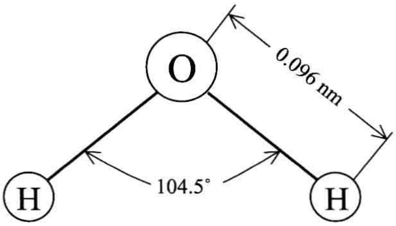

Fig. 1.1. Structure of a water molecule.

For the electronic polarizability of water (divided, as is conventional, by $4\pi\varepsilon_0$, where ε_0 is the permittivity of vacuum), we recommend the value $1.457(3) \times 10^{-30}$ m^3 (Russell and Spackman, 1995). Bishop and Cheung (1982) estimated a vibrational contribution in the low-frequency limit of 0.037×10^{-30} m^3, with an uncertainty near 10%. Combining these values gives $1.494(7) \times 10^{-30}$ m^3 for the mean total dipole polarizability in the static limit.

1.2.2. Microscopic Structure of Bulk Water

The key feature of water's microscopic structure is hydrogen bonding. Because of the geometry and charge distribution of the water molecule, it tends to favor tetrahedral coordination with its neighbors, where each hydrogen atom is aligned between the oxygen atom to which it is covalently bonded and an oxygen atom on another molecule. This produces a highly directional bonding interaction with a strength near 20 kJ·mol^{-1}, which, while weaker than a true chemical bond, is stronger than typical intermolecular forces. The tetrahedral coordination is nearly perfect in ice; in fluid water, it is manifested as a local tendency for groups of molecules to adopt hydrogen-bonded configurations more often than if they were randomly oriented. At higher temperatures, the thermal energy produces more random configurations, so the amount of hydrogen bonding decreases with temperature. Nevertheless, some hydrogen bonding persists at high temperatures, even above 700 K. The microscopic structure of water will be discussed in detail in Chapter 5.

1.2.3. Isotopic Composition

Because hydrogen and oxygen exist in nature as different isotopes, the isotopic composition must be specified in order to completely describe a particular sample of 'water'. Hydrogen's stable isotopes are those of mass numbers 1 (^{1}H) and 2 (^{2}H, commonly written D and called deuterium). Oxygen's stable isotopes are ^{16}O, ^{17}O, and ^{18}O.

In nature, water consists almost entirely of ^{1}H and ^{16}O. Because certain natural processes (such as evaporation and precipitation) produce a slight fractionation between water molecules containing different isotopes, scientists can use isotopic compositions to trace processes such as global atmospheric circulation. Application of stable isotope partitioning in industrial settings is discussed in Chapter 9. In order to have a baseline for such studies, and in order to provide a standard for high-precision measurements, it is necessary to define a standard isotopic composition for water. The international standard is called Vienna Standard Mean Ocean Water (VSMOW) (Craig, 1961; Gonfiantini, 1978; NIST, 1992). Water obtained from deep in the oceans is remarkably uniform worldwide in its isotopic composition; the composition of VSMOW (listed in Table 1.1) is chosen to duplicate that composition. International standards for the properties of water (sometimes called 'ordinary water substance' for historical reasons) can be

Table 1.1. Isotopic composition of Vienna Standard Mean Ocean Water (NIST, 1992)

Isotope	Mass ($g \cdot mol^{-1}$)	Atom %
^{1}H	1.00782503214	99.984426
^{2}H	2.01410177799	0.015574
^{16}O	15.9949146621	99.76206
^{17}O	16.99913150	0.03790
^{18}O	17.99916038	0.20004
Molar mass (VSMOW)	18.015268	
Molar mass (D_2O)	20.027508	

Isotopic masses from Audi and Wapstra (1995).

assumed to be for VSMOW, although it is only for the most precise property data that differences due to isotopic composition are significant.

From the composition in Table 1.1 and the known masses of the isotopes (Audi and Wapstra, 1995), it is straightforward to calculate the molar mass (commonly called the 'molecular weight') of VSMOW. The resulting molar mass is 18.015268 $g \cdot mol^{-1}$. This is the value that should be used when converting water property representations between a mass basis and a molar basis, unless there is specific knowledge that the water to which the calculation is being applied has a different isotopic composition.

Heavy water (D_2O) is also produced and used for various purposes. The standard definition of 'heavy water' is water whose hydrogen is 100% deuterium, and whose oxygen has the isotopic composition of VSMOW (Kell, 1977). With this definition, the calculation of molar mass can be repeated for D_2O, yielding a value of 20.027508 $g \cdot mol^{-1}$.

1.2.4. Ideal-Gas Properties

There is no such thing as an 'ideal' gas; it is a hypothetical construct in which there are no interactions between molecules. However, at sufficiently low densities most substances (including water) behave nearly as ideal gases. In addition, models for the properties of real fluids often use the ideal gas as a starting point. It is, therefore, useful to be able to describe accurately the thermodynamic properties of water in the ideal-gas state.

The volumetric behavior of any ideal gas is given by $p/\rho RT = 1$, where p is the pressure, ρ is the molar density, R is the molar gas constant, and T is the absolute temperature. Differences in molecular structure cause differences in energy-related properties (enthalpy, heat capacity, *etc.*) among different substances in the ideal-gas state. These properties can be estimated from calorimetric or acoustic measurements at low densities, but more often they are obtained from statistical mechanics and knowledge of the rotational and vibrational states of the molecule.

Table 1.2. Coefficients for Eq. 1.1

i	b_i	β_i/K
0	4.00632	
1	0.012436	833
2	0.97315	2289
3	1.2795	5009
4	0.96956	5982
5	0.24873	17 800

Information about molecular rotation and vibration can be obtained from spectroscopy and/or calculated from quantum mechanics; for water there are good spectroscopic data. The statistical–mechanical calculations lead to a molar isobaric heat capacity c_p, which can be integrated to obtain other energy-related properties of the ideal gas. For water, a representation covering temperatures from 130 to 2000 K is given by Cooper (1982):

$$\frac{c_p}{R} = b_0 + \sum_{i=1}^{5} b_i \frac{x_i^2 \exp(-x_i)}{(1 - \exp(-x_i))^2}, \tag{1.1}$$

where $x_i = \beta_i/T$ and coefficients b_i and β_i are listed in Table 1.2. A more recent thorough computation of water's ideal-gas heat capacity (Vidler and Tennyson, 2000) produces values that differ slightly from Eq. 1.1, but the discrepancy is negligible below 1000 K and is less than 0.5% over the entire range of validity of Eq. 1.1.

1.2.5. Second Virial Coefficient

The second virial coefficient B is the first correction to the ideal-gas law in the expansion

$$p/\rho RT = 1 + B\rho + C\rho^2 + \cdots \tag{1.2}$$

It is a rigorous result of statistical mechanics that B depends only on the interaction between two molecules of the substance in question. B is a function of temperature only, and is typically obtained by measuring the pressure as a fixed amount of gas is expanded isothermally into known volumes.

For water, the usual experiments are complicated below about 500 K by adsorption on the surfaces of the apparatus; as a result, the extraction of second virial coefficients from experimental data is quite difficult. Harvey (2000) concluded that, at the temperatures where adsorption is significant, the most accurate experimental values were those of Eubank *et al.* (1988) and Kell *et al.* (1989). Information on the derivative $\mathrm{d}B/\mathrm{d}T$ may be obtained from Joule–Thomson expansion experiments such as those of McGlashan and Wormald (2000). Harvey and Lemmon (2004) analyzed the available data and produced a correlation for $B(T)$ between approximately 310 and 1170 K.

1.3. Phase Diagram of Water

Most people are at least qualitatively familiar with the transitions of water among vapor, liquid, and solid phases. It is customary and useful to represent this information with a *phase diagram*, which is a plot of pressure *versus* temperature with the regions designated where each phase is the equilibrium state. A phase diagram of water is shown in Fig. 1.2 (note the logarithmic pressure scale).

1.3.1. Solid–Fluid Equilibria and the Triple Point

The starting point for discussion of the phase diagram is the *triple point*, the unique condition where solid, liquid, and vapor coexist. This is the point (labeled 'T') in Fig. 1.2 where three curves intersect. The temperature at the triple point of ordinary water is exactly 273.16 K; this is a part of the definition of the absolute temperature scale (Preston-Thomas, 1990). The most precise measurement of

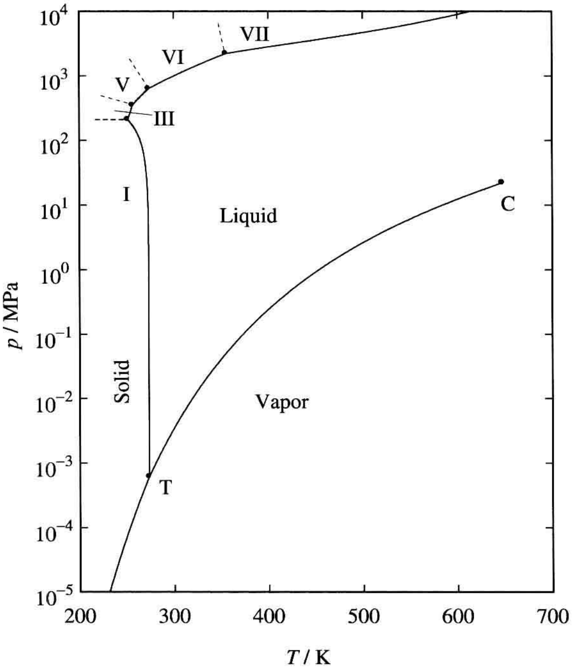

Fig. 1.2. Phase diagram of water (C = critical point; T = triple point).