



AQUEOUS SYSTEMS AT ELEVATED TEMPERATURES AND PRESSURES

Donald A. Palmer

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Physical Chemistry in Water, Steam
and Hydrothermal Solutions

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Physical Chemistry in Water, Steam
and Hydrothermal Solutions

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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/cm³ 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, because 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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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.

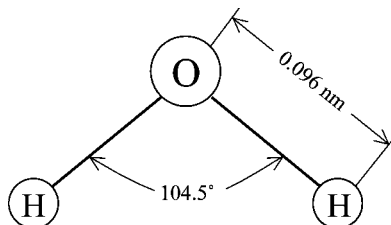


Fig. 1.1. Structure of a water molecule.

For the electronic polarizability of water (divided, as is conventional, by $4\pi\epsilon_0$, where ϵ_0 is the permittivity of vacuum), we recommend the value $1.457(3) \times 10^{-30} \text{ m}^3$ (Russell and Spackman, 1995). Bishop and Cheung (1982) estimated a vibrational contribution in the low-frequency limit of $0.037 \times 10^{-30} \text{ m}^3$, with an uncertainty near 10%. Combining these values gives $1.494(7) \times 10^{-30} \text{ m}^3$ 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 $20 \text{ kJ}\cdot\text{mol}^{-1}$, 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 (^1H) and 2 (^2H , 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 ^1H 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 ($\text{g}\cdot\text{mol}^{-1}$)	Atom %
^1H	1.00782503214	99.984426
^2H	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 $18.015268 \text{ g}\cdot\text{mol}^{-1}$. 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 $20.027508 \text{ g}\cdot\text{mol}^{-1}$.

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):

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

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

$$p/\rho RT = 1 + B\rho + C\rho^2 + \dots \quad (1.2)$$

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 dB/dT 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

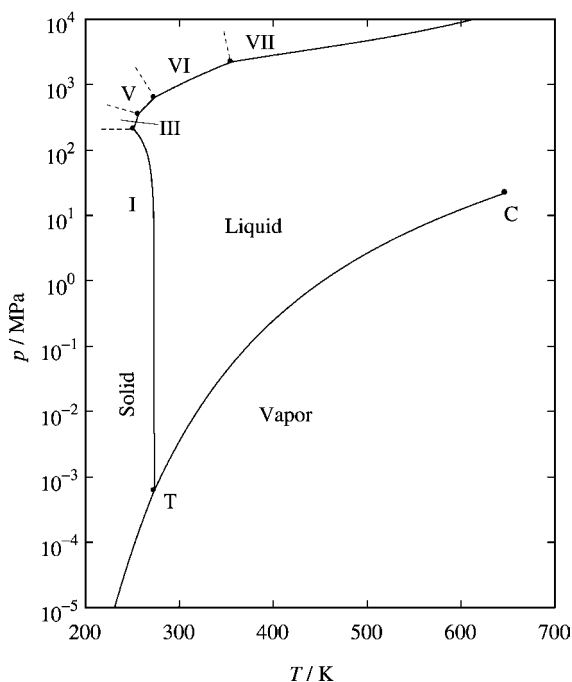


Fig. 1.2. Phase diagram of water (C = critical point; T = triple point).

the pressure at water's triple point gives a value of 611.657 ± 0.010 Pa (Guildner *et al.*, 1976).

At pressures below the triple-point pressure, the only equilibrium phases that can exist are the solid (ice) and vapor phases. The vapor pressure (also called sublimation pressure) of ice in this region has been measured to some extent, and can also be inferred from other thermodynamic data. A representation for temperatures from 190 to 273.16 K is given by Wagner *et al.* (1994):

$$\ln\left(\frac{p_{\text{subl}}}{p_t}\right) = a_1(1 - \theta_t^{-1.5}) + a_2(1 - \theta_t^{-1.25}), \quad (1.3)$$

where $\theta_t = T/T_t$, $T_t = 273.16$ K, $p_t = 611.657$ Pa, $a_1 = -13.928169$, and $a_2 = 34.7078238$.

At pressures above the triple point, the solid coexists with the liquid. As the pressure is increased, the solid–liquid boundary initially goes to lower temperatures. This negatively sloped melting curve is a thermodynamic consequence of the fact that ice (as ice I, the stable form at lower pressures) is less dense than liquid water. At higher pressures, other forms of ice (with different crystal structures, designated by Roman numerals) become stable, as shown in Fig. 1.2. Since these forms are more dense than the coexisting liquid water, the slope of the melting curve becomes positive. Wagner *et al.* (1994) give the locations of the points on the melting curve corresponding to transitions between two forms of ice, and also give equations for the solid–liquid boundaries. There are also solid–solid transitions between ice forms, but those are outside the scope of this work. We refer the reader elsewhere for information on the properties of ice (Franks, 1972; Wexler, 1977; Hyland and Wexler, 1983; Fukusako, 1990).

1.3.2. Vapor–Liquid Equilibria and the Critical Point

The most important aspect of the phase diagram for most purposes is the coexistence between vapor and liquid, commonly known as the vapor-pressure curve. The vapor pressure increases with temperature, until a point is reached where the liquid (expanded with increasing temperature) and the vapor (compressed by the higher pressure) become identical. This terminus of the vapor-pressure curve (marked by a ‘C’ on Fig. 1.2) is called the *critical point*. Some thermodynamic properties (such as the isothermal compressibility) diverge toward infinity at the critical point. The special character of fluid behavior near the critical point will be discussed in Chapter 2. Careful analysis of available data has led IAPWS to recommend values for the temperature, pressure, and density of water at its critical point (Levelt Sengers *et al.*, 1985; IAPWS, 1992); these values and their uncertainties (along with the corresponding values for heavy water) are listed in Table 1.3.

The vapor-pressure curve of water has long been an object of study, going back to the steam-engine work of Watt in the 1700s. The vapor pressure is now known

Table 1.3. Critical constants for H₂O and D₂O

	H ₂ O	D ₂ O
T_c (K)	$647.096 + \delta_1$ ($\delta_1 = 0.0 \pm 0.100$)	$643.847 + \delta_2$ ($\delta_2 = 0.0 \pm 0.200$)
p_c (MPa)	$22.064 + 0.27\delta_1 \pm 0.005$	$21.671 + 0.27\delta_1 \pm 0.010$
ρ_c (kg·m ⁻³)	322 ± 3	356 ± 5

to within approximately 0.025% at most temperatures, with somewhat smaller uncertainties near the triple point and normal boiling point. An equation representing the vapor pressure p^s within this uncertainty has been given by Wagner and Pruss (1993):

$$\ln(p^s/p_c) = (T_c/T)(a_1\tau + a_2\tau^{1.5} + a_3\tau^3 + a_4\tau^{3.5} + a_5\tau^4 + a_6\tau^{7.5}), \quad (1.4)$$

where $\tau = 1 - T/T_c$, T_c and p_c are listed in Table 1.3, and the coefficients a_1 to a_6 are listed in Table 1.4.

The vapor pressure of water at a given temperature is lower than that of other substances (such as H₂S and NH₃) that one might expect to behave similarly based on their molecular formulas. This is a consequence of the strong hydrogen bonding in liquid water; these interactions increase the amount of thermal energy required to remove molecules from the liquid to the vapor.

1.3.3. Supercritical Region

Another region of the phase diagram that is referred to in some contexts is the ‘supercritical’ region. Unfortunately, there is no uniform definition of this term. It always refers to a condition where the temperature is above the critical temperature T_c . Some use it to refer to any system above T_c , regardless of the pressure, while others restrict use of the term to the region where both the temperature and pressure are above their critical values. At temperatures above T_c , it is possible to go from liquid-like densities to vapor-like densities by changing pressure without passing through a phase transition; this has potential advantages

Table 1.4. Coefficients for Eq. 1.4

i	a_i
1	-7.85951783
2	1.84408259
3	-11.7866497
4	22.6807411
5	-15.9618719
6	1.80122502

for some separation processes. Several subsequent chapters will discuss aspects of physical chemistry in supercritical water.

1.3.4. Metastable States

Figure 1.2 illustrates only the equilibrium phases of water. However, it is possible for water to exist for significant periods of time in states where it is not in thermodynamic equilibrium. Such states are referred to as *metastable*. A familiar metastable state is the *superheated liquid*, which can be obtained by heating water in a smooth container. If the liquid is not disturbed, it can be brought to a temperature well above its boiling point. Until boiling begins (a process known as nucleation), the liquid is in a metastable state that is physically indistinguishable from an ordinary liquid, except that given sufficient time it will attain its equilibrium state corresponding to its position in relation to the equilibrium phase boundary. Similarly, one can produce a *supercooled liquid* by careful cooling below the freezing temperature. Supercooled liquids, and supercooled water in particular, have interesting properties that are an active area of research. We refer readers to a review (Stanley *et al.*, 2000) for details. Vapors can also be metastable; a *supersaturated vapor* is one that has been cooled to a temperature where the equilibrium state would be a liquid at the pressure of the system. Supersaturated steam is important in steam turbines, where the time scales of the expansions are so short that at some points the steam is supersaturated because it has not had time to condense. Nucleation in these systems is discussed in Chapter 7.

1.4. Thermodynamic Properties

1.4.1. Background

It is common to consider two basic categories of thermodynamic properties of fluids. *Volumetric* properties refer to the relationship between the molar volume v (or the molar density $\rho = 1/v$), the pressure p , and the (absolute) temperature T . They would also include such ‘derivative’ properties as the isothermal compressibility, $-(1/v)(\partial v/\partial p)_T$. *Caloric* properties refer to the amount of thermal energy that must be added to or removed from a fluid to change its state. The molar internal energy u or the molar isochoric heat capacity c_v would be examples of caloric properties. Often, properties of practical interest are combinations of volumetric and caloric properties, such as the molar enthalpy $h = u + pv$ or molar Gibbs energy $g = h - Ts$ (where s is the molar entropy). Since the definitions of thermodynamic properties and the relationships among them can be found in a multitude of textbooks, we will not detail them here.

Historically, the thermodynamic properties of water and steam have most often been presented in the form of printed ‘steam tables’. By the early 1900s,

the growing use of steam for electric power generation increased the demand for tabulations of the enthalpy, entropy, and volume of water and steam both at vapor–liquid saturation and in single-phase states. Unfortunately, different steam tables often disagreed significantly, especially at higher temperatures. This made it difficult for industry to compare designs and evaluate the performance of equipment. As a result, a series of international conferences was organized, leading to the adoption in 1934 of a single set of ‘skeleton tables’ with agreed-upon values for key thermodynamic properties and their uncertainties. The current IAPWS is the successor to those conferences.

1.4.2. Thermodynamic Property Formulations

Now that the use of computers is widespread, printed tables are less useful. What is usually desired instead is a formulation that can be programmed into a computer and used for any calculation of interest. As a result, current IAPWS standards are in the form of equations.

IAPWS has two different (but closely related) standard formulations for the thermodynamic properties of water; these are intended to serve two different audiences. For much use in industry and almost all use in science, the most accurate properties possible should be used. However, the steam power industry (in which ‘steam tables’ first became important) has some special needs. Small changes in calculated thermodynamic properties will affect calculated efficiencies, heat rates, *etc.* by an economically significant amount. Because contracting and equipment evaluation are so closely tied to these factors, changing the formulation used requires great care and effort. Therefore, the power industry needs a formulation that remains unchanged for many years. In addition, calculations such as finite-element computations of flows in turbines require millions of calls to water properties, making it desirable to have a formulation designed for fast computing. For these needs, IAPWS has a special standard for ‘industrial use’. This standard was adopted in 1997 (replacing the previous formulation that was adopted in 1967), and is intended to remain in place for approximately 30 years. The formulation for industrial use, known as IAPWS-IF97, has been described in detail elsewhere (Wagner *et al.*, 2000) and has been the basis for books of ‘steam tables’ (Wagner and Kruse, 1998; Parry *et al.*, 2000); thus, we will not discuss it further here.

In this book on aqueous physical chemistry, it is appropriate to concentrate on the IAPWS formulation ‘for general and scientific use’. The current standard formulation (IAPWS, 1996; Wagner and Pr  , 2002) was adopted in 1995; we will refer to it as IAPWS-95. The formulation is constructed as a single equation for the specific (per unit mass) Helmholtz energy as a function of temperature and density. From this equation, appropriate differentiation and manipulation can produce any equilibrium thermodynamic property of the fluid. One may compute vapor–liquid equilibria by equating the Gibbs energies of the two phases.

1.4.3. Behavior of Thermodynamic Properties

Vapor–liquid equilibria, and the values of thermodynamic properties of the saturated vapor and saturated liquid, are of the most interest. The vapor pressure as a function of temperature is described by Eq. 1.4. Equations have also been derived (Wagner and Pruss, 1993) for the most important thermodynamic properties (density, enthalpy, entropy) for the saturated liquid and saturated vapor.

The densities of the saturated liquid and vapor, ρ' and ρ'' , are given by

$$\rho'/\rho_c = 1 + b_1\tau^{1/3} + b_2\tau^{2/3} + b_3\tau^{5/3} + b_4\tau^{16/3} + b_5\tau^{43/3} + b_6\tau^{110/3}, \quad (1.5)$$

$$\ln(\rho''/\rho_c) = c_1\tau^{2/6} + c_2\tau^{4/6} + c_3\tau^{8/6} + c_4\tau^{18/6} + c_5\tau^{37/6} + c_6\tau^{71/6}, \quad (1.6)$$

where $\tau = 1 - T/T_c$, T_c and ρ_c are listed in Table 1.3, and the coefficients b_i and c_i are listed in Table 1.5. In order to compute enthalpies and entropies at saturation, the auxiliary quantities α and ϕ are defined by

$$\alpha/\alpha_0 = d_\alpha + d_1\theta^{-19} + d_2\theta + d_3\theta^{4.5} + d_4\theta^5 + d_5\theta^{54.5}, \quad (1.7)$$

$$\phi/\phi_0 = d_\phi + \frac{19}{20}d_1\theta^{-20} + d_2\ln\theta + \frac{9}{7}d_3\theta^{3.5} + \frac{5}{4}d_4\theta^4 + \frac{109}{107}d_5\theta^{53.5}, \quad (1.8)$$

where $\theta = T/T_c$, $\alpha_0 = 1000 \text{ J}\cdot\text{kg}^{-1}$, $\phi_0 = \alpha_0/T_c$, $d_\alpha = -1135.905627715$, $d_\phi = 2319.5246$, and d_1 to d_5 are listed in Table 1.5. The values of d_α and d_ϕ are chosen to satisfy the convention that the internal energy and entropy are assigned a value of zero for the saturated liquid at the triple point. The enthalpies of the saturated liquid and vapor, h' and h'' , and the saturated liquid and vapor entropies s' and s'' , are then given by

$$h' = \alpha + \frac{T}{\rho'} \frac{dp^s}{dT}, \quad (1.9)$$

$$h'' = \alpha + \frac{T}{\rho''} \frac{dp^s}{dT}, \quad (1.10)$$

Table 1.5. Coefficients for Eqs. 1.5–1.8

i	b_i	c_i	d_i
1	1.99274064	-2.03150240	$-5.65134998 \times 10^{-8}$
2	1.09965342	-2.68302940	2690.66631
3	-0.510839303	-5.38626492	127.287297
4	-1.75493479	-17.2991605	-135.003439
5	-45.5170352	-44.7586581	0.981825814
6	-6.74694450×10^5	-63.9201063	

$$s' = \phi + \frac{1}{\rho'} \frac{dp^s}{dT}, \quad (1.11)$$

$$s'' = \phi + \frac{1}{\rho''} \frac{dp^s}{dT}, \quad (1.12)$$

where dp^s/dT , the derivative of the vapor-pressure curve, is obtained by differentiating Eq. 1.4. While Eqs. 1.5–1.12 give slightly different values for the saturation properties than those obtained (at much more computational expense) by solving for the saturation boundary from the full IAPWS-95 formulation for thermodynamic properties, the differences are much smaller than the uncertainties in the formulations. It should be noted that Eqs. 1.5–1.12 yield properties on a mass (as opposed to a molar) basis.

To illustrate the behavior of properties over the entire fluid range, we will use figures in which the property is calculated (from the IAPWS-95 formulation) as a function of temperature for several different pressures. To illustrate a variety of conditions, we choose one relatively low pressure (usually 0.1 MPa, close to standard atmospheric pressure), one high pressure below p_c (10 MPa), one pressure slightly above p_c (22.1 MPa) to illustrate interesting near-critical behavior, and one supercritical pressure (100 MPa). We also show the values for the saturated liquid and saturated vapor as a function of temperature.

We begin with volumetric behavior. Figure 1.3 shows the density along four isobars and at saturation. The vapor density at 0.1 MPa is too close to zero to be visible on the scale of the figure. At low temperatures, the liquid density does not change greatly with pressure; this reflects the small compressibility of liquid water. The liquid expands considerably at higher temperatures; many properties of water (including its behavior as a solvent) are significantly affected by this change in density. A final noteworthy feature is the nearly vertical slope of the near-critical isobar, where a small change in temperature (or pressure) causes a large change in density. This reflects the divergence of the isothermal compressibility, $-(1/\nu) \times (\partial\nu/\partial p)_T$, and the volume expansivity, $(1/\nu)(\partial\nu/\partial T)_p$, at the critical point.

Figure 1.4 shows a similar plot for the enthalpy. The enthalpy of vaporization (the difference between the enthalpies of the saturated vapor and liquid) is about $2500 \text{ kJ}\cdot\text{kg}^{-1}$ at the triple point, gradually declining to zero (with a steeper decline near the critical point) as the temperature is increased. The liquid enthalpy is relatively insensitive to pressure. The slopes of the isobars on this plot correspond to the isobaric heat capacity c_p . In general, a higher density leads to a higher value of c_p (due to the intermolecular interactions); for example, the liquid heat capacity at low temperatures is about twice that of the low-pressure vapor (which would be nearly identical to the ideal-gas value given by Eq. 1.1). The decline in the saturated vapor enthalpy at high temperatures is common to all fluids, but is sometimes misunderstood. It does not mean that the vapor has a negative heat capacity; the isobaric heat capacity c_p is defined with pressure held constant, and

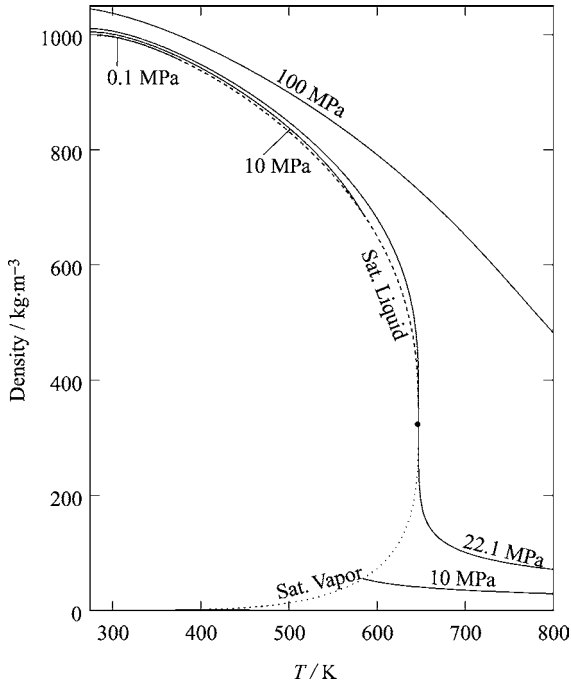


Fig. 1.3. Density of water.

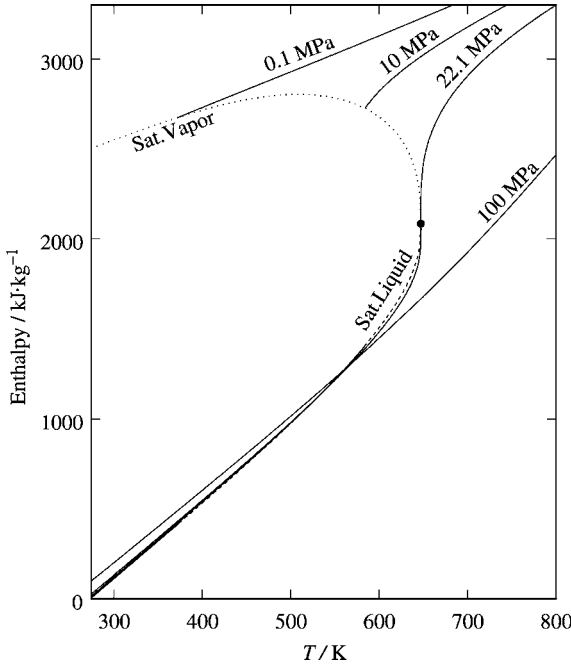


Fig. 1.4. Enthalpy of water.

this constancy condition is not maintained when the path is along the saturation curve. The near-vertical slope of the 22.1 MPa isobar reflects the divergence of c_p at the critical point.

Another thermodynamic property of some interest is the speed of sound, whose behavior is illustrated in Fig. 1.5. The maxima in the liquid isobars are caused by two competing effects. In general, an increase in temperature increases the speed of propagation of sound waves. However, sound waves propagate more slowly at lower density (as evidenced by the lower values for the vapor). As the temperature of the liquid is increased from near freezing, the first effect is initially more important, but eventually the decrease in liquid density at higher temperatures dominates, and the speed of sound begins to decline. Comparing with Fig. 1.3, we see that the effect of pressure on the speed of sound for the liquid is more pronounced than its effect on the density. Figure 1.5 also shows the decline in the speed of sound near the critical point (where theory dictates that it reaches zero).

For engineering and scientific use, it is important to know not only the values of the various thermodynamic properties, but also the degree of accuracy to which they are known. The relevant uncertainties, which are primarily dictated by the quality of the data to which the formulation was fit, are given in both the IAPWS Release (IAPWS, 1996) and the corresponding journal article (Wagner and Pruß, 2002). Briefly, the uncertainties are quite small for the liquid near room temperature and atmospheric pressure (on the order of 0.0001% for the density, 0.1% for c_p , and 0.005% for the speed of sound), and generally increase at higher temperatures and pressures (and also near the critical point).

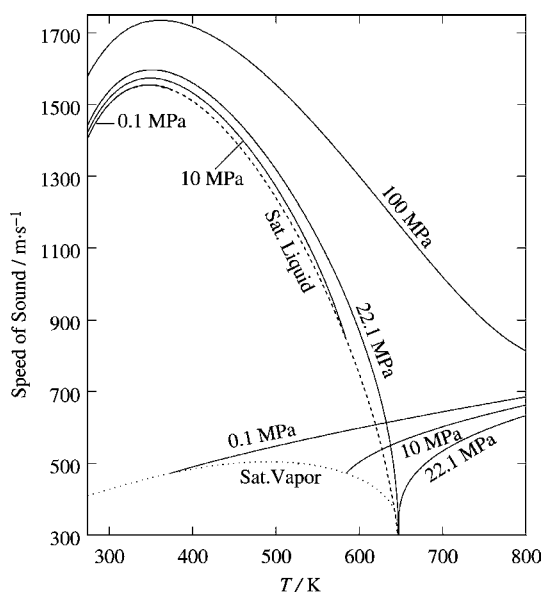


Fig. 1.5. Speed of sound in water.

Special mention should be made of the density of liquid water near room temperature, which is of particular importance as a standard for calibrations and other metrology applications. For this reason, the CCM (Consultative Committee for Mass and Related Quantities) of the CIPM (Comité International des Poids et Mesures) has adopted standard densities for water of standard isotopic composition (VSMOW) for temperatures from 0 to 40 °C at a standard pressure of 101.325 kPa (Tanaka *et al.*, 2001). Procedures are given for correcting these densities for the effects of small changes in pressure and isotopic composition, and for the presence of dissolved air. While the IAPWS-95 formulation is in agreement with the CIPM densities within their mutual uncertainties, the latter are preferred for metrology applications in the limited region where the CIPM representation is valid.

While the IAPWS-95 formulation is primarily intended for stable fluid states, it can also be used to calculate thermodynamic properties for metastable states. In most cases, these calculations are physically reasonable and in agreement with the limited data available (Wagner and Pruß, 2002). For the subcooled vapor, however, it is believed that IAPWS-95 does not give the best values, and a special equation for the metastable vapor contained in the IAPWS-IF97 ‘industrial’ formulation (Wagner *et al.*, 2000) is recommended instead.

1.5. Transport Properties

1.5.1. Viscosity

The viscosity of a fluid is a measure of its ability to transfer momentum across the direction of flow in a non-equilibrium situation. One can think, for instance, of the resistance to stirring in a liquid, or a measure of the resistance to any shearing force. In the simplest linear and symmetric case, the viscosity is defined by

$$\frac{f}{A} = -\eta \frac{du}{dz}, \quad (1.13)$$

where η is the viscosity, f/A is the force (*i.e.*, the time rate of change of momentum) per unit area, u is the fluid speed in the direction of flow, and z is a coordinate perpendicular to the direction of flow.

For fluid water in most common situations, the behavior is Newtonian, meaning that the viscosity is independent of the magnitude of the shear (du/dz). It does, however, depend on the temperature and density of the fluid. As with most fluids, the viscosity of water depends weakly on temperature and strongly on density. Note that the viscosity has dimensions of pressure times time, so it is measured in Pa·s (the obsolete unit of ‘poise’ will not be used here).

The viscosity defined by Eq. 1.13 is also called the *dynamic viscosity*. The *kinematic viscosity* is defined as the ratio of the dynamic viscosity to the mass

density, η/ρ , with units of $\text{m}^2\cdot\text{s}^{-1}$. This combination of variables is useful in many fluid-flow applications, but we will not discuss it further here because it is easily calculated from the dynamic viscosity and the density.

IAPWS has developed and maintains a standard formulation for the viscosity of water as a function of temperature and density (IAPWS, 2003). The 2003 IAPWS release for viscosity provides the equations, which will not be repeated here. Note that this 2003 document represents only minor changes from a 1985 IAPWS document; study of new data in the intervening years and development of a new IAPWS standard is currently underway. Water is an important calibration fluid for viscometry (the measurement of viscosity), and the International Standards Organization (ISO) provides a standard value for the viscosity of water at 20 °C and 101.325 kPa (standard atmospheric pressure); this calibration value is 1.0016 mPa·s, with an uncertainty of 0.17% (ISO, 1998). This value agrees with the result calculated from the IAPWS viscosity formulation.

The uncertainty in the IAPWS formulation is specified by tables giving the uncertainty of the viscosity for a grid of temperature–pressure state points as determined from the available data. In general, these uncertainties range from about 1 to 3% in the broad region covered by the formulation.

Figure 1.6 shows the viscosity of water, both along the liquid–vapor saturation boundaries and along isobars. The general behavior of the viscosity of water is

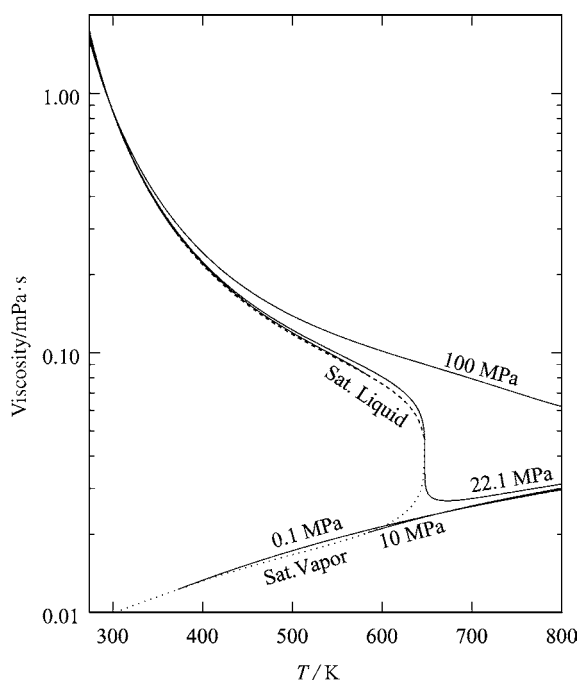


Fig. 1.6. Viscosity of water.

similar to that for other fluids: most importantly, the viscosity of the liquid phase is much higher than that of the vapor. Note that a logarithmic scale was used to include the high viscosities for the low-temperature liquid. At a fixed pressure, the liquid viscosity generally decreases with increasing temperature, and the opposite is true for the vapor. For the vapor phase, Fig. 1.6 shows the ‘inversion’ of the pressure-dependence of the isotherms at low temperatures; namely, increasing the pressure results in a lower viscosity along the low-temperature vapor isotherms. In fact, this low-pressure behavior can be found for most fluids at both low and high temperatures (where ‘low’ and ‘high’ are relative to the critical temperature of the fluid). For the liquid phase, the relative incompressibility at low temperatures is again seen; as the density changes very little with pressure, the isobars of viscosity are closely spaced, so that the viscosity at 100 MPa is close to that for the saturated liquid. At low temperatures (near 300 K), the isobars cross, so that the lower-pressure liquid state (at a given temperature) has a higher viscosity. This anomaly is shown in Fig. 1.7, where the liquid viscosity at 300 K is plotted *versus* density. The density, and therefore, the viscosity change with applied pressure, with the minimum viscosity near 40 MPa. This is a rather shallow minimum, as indicated by the scale of the viscosity axis.

As a final issue related to the behavior of the viscosity of water, we mention the critical region. The density fluctuations associated with criticality affect

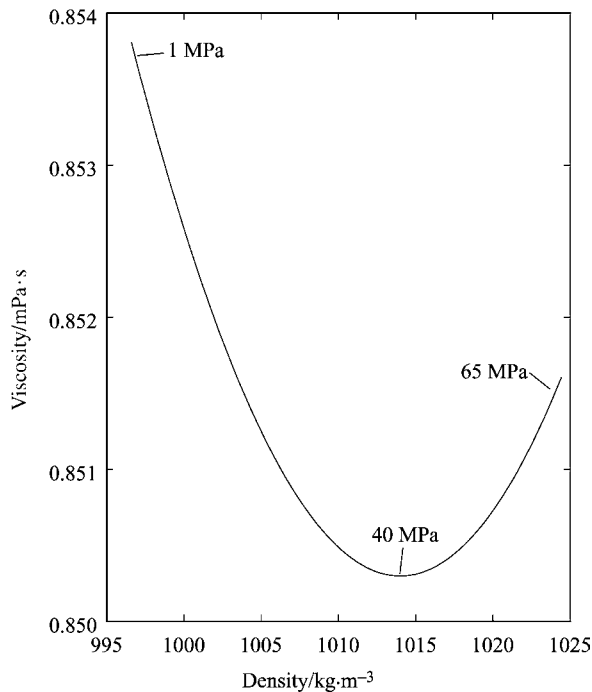


Fig. 1.7. Viscosity of water at 300 K.

the viscosity; however, the critical anomaly in the viscosity is rather slight, being significant only for states extremely close to the critical point, so it is not visible within the resolution of Fig. 1.6. This divergence, and the much stronger near-critical effect on the thermal conductivity, are discussed in Chapter 2.

1.5.2. Thermal Conductivity

The thermal conductivity of a fluid is a measure of its ability to transfer heat via a temperature gradient. The quantity of energy flowing by conduction is generally linearly proportional to the gradient, and Fourier's law of conduction is given by

$$J_Q = -\lambda \frac{dT}{dz}, \quad (1.14)$$

where J_Q is the heat flux (energy per unit time per unit area), λ is the thermal conductivity, and dT/dz is the temperature gradient.

The thermal conductivity is usually independent of the magnitude of the temperature gradient, but depends on the temperature and density. It is important to note that for many common heat transfer problems, convection (transfer of heat through the macroscopic motion of the fluid) and radiation (transfer of heat by electromagnetic means) are active, as well as conduction of heat (which is a molecular-scale phenomenon). The thermal conductivity is directly related only to conductive heat transfer. The units of thermal conductivity are watts per meter per kelvin ($\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$).

In this context, two other properties related to heat transfer should also be mentioned. The *thermal diffusivity* is associated with energy balance in heat conduction problems; it couples the energy-storage mechanism (related to heat capacity) with the thermal conductivity and is defined by $\lambda/(\rho c_p)$, where ρ is the fluid density and c_p is the isobaric heat capacity. The *Prandtl number* is often needed when viscous heating is of interest; this dimensionless quantity is defined by $c_p \eta / \lambda$ and is the ratio of the kinematic viscosity to the thermal diffusivity.

IAPWS has also developed and maintains standard formulations for the thermal conductivity of water as a function of temperature and density (IAPWS, 1998). The 1998 IAPWS release for thermal conductivity provides these equations, which will not be repeated here. Two sets of equations for the thermal conductivity have been adopted: a computationally simpler formulation meant for industrial use, and the equations for general and scientific use that are the focus of this discussion. The IAPWS document includes only minor revisions of the equations developed for a 1985 release; as for the viscosity, work is currently underway toward the development of a new IAPWS standard for the thermal conductivity.

The uncertainty in the IAPWS formulation, tabulated in the release for a specified grid of temperature and pressure as well as in a table for the saturation

boundary, is generally estimated as 1.5–4%. However, near the critical point, the uncertainty is considerably higher.

Figure 1.8 shows the general trends in the thermal conductivity of water along four isobars and along the vapor and liquid saturation boundaries. Although the behavior of the vapor-phase thermal conductivity is similar to that of other fluids, the liquid is unusual. As for the viscosity, the behavior of the isobars in the low-temperature region follows the trend seen for the saturated liquid (where the density decreases as the temperature is increased). While most fluids show a decrease in thermal conductivity with increase of temperature along the saturated liquid (well below the critical temperature), water exhibits a maximum value near 400 K. Below this temperature, the isobaric thermal conductivity *versus* temperature curves have a positive slope; this behavior may be related to the temperature dependence of the hydrogen-bonding phenomenon.

The critical divergence of the thermal conductivity is manifested in water, as with most fluids, by an anomalous increase in a very broad region around the critical point. This is visible in Fig. 1.8 on the phase boundary as well as along the 22.1 MPa isobar. Unlike the related divergence of the viscosity, the divergence in the thermal conductivity is significant in a large enough region that it cannot be ignored for practical calculations (see Chapter 2).

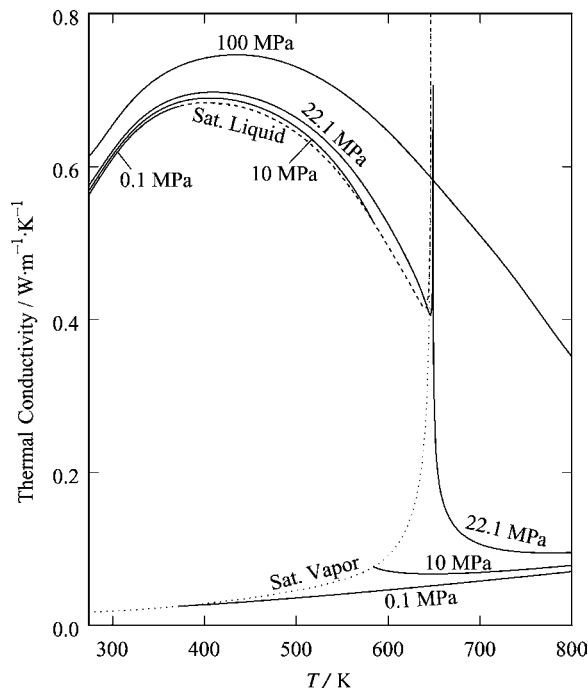


Fig. 1.8. Thermal conductivity of water.

1.5.3. Self-Diffusion Coefficient

The other commonly studied fluid transport process besides momentum transfer (described by the viscosity) and heat transfer (described by the thermal conductivity) is mass transfer, described by the diffusivity. Most practical interest involves the diffusion of solutes in water, which is beyond the scope of this chapter (diffusion of aqueous ionic species is discussed in Chapter 10). However, the self-diffusion coefficient of pure water is of some interest in its own right. The accepted value for liquid water near atmospheric pressure at 25 °C is approximately $2.3 \times 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$; recommended values from 0 to 100 °C are given by Holz *et al.* (2000) and a correlation for the liquid at higher temperatures is given by Easteal *et al.* (1989). The effect of pressure on self-diffusion in liquid water is summarized by Weingärtner (1982). At higher temperatures and lower densities such as those found at supercritical conditions, the diffusivity is much higher; this can have implications in areas such as reaction kinetics. Self-diffusion in compressed supercritical water has been measured by Lamb *et al.* (1981).

1.5.4. Electrical Conductivity

Even pure water is able to conduct electricity to a very slight extent due to its self-ionization. The conductivity of a sample of water is commonly used as a measure of its purity; perfect purity corresponds to a conductivity of approximately $0.055 \mu\text{S} \cdot \text{cm}^{-1}$ for the liquid at 25 °C. The electrical conductivity of pure water is closely related to its ionic dissociation constant (see below); that relationship has been exploited to produce a formulation for the conductivity that extends to high temperatures and pressures (Marshall, 1987).

1.6. Miscellaneous Properties

1.6.1. Surface Tension

The vapor–liquid surface tension of water is somewhat higher than that of most organic and inorganic liquids. For example, water’s surface tension at 300 K is about $71.7 \text{ mN} \cdot \text{m}^{-1}$, compared to $20\text{--}40 \text{ mN} \cdot \text{m}^{-1}$ for typical organic liquids. The data for the surface tension of water have been carefully evaluated (Vargaftik *et al.*, 1983) and are correlated in an IAPWS Release (IAPWS, 1994a). It should be noted that the ‘calculated’ values printed in the 1994 reference are incorrect; corrected numbers are given in the Release document on www.iapws.org. The equation for the surface tension σ is

$$\sigma = B\tau^\mu(1 + b\tau), \quad (1.15)$$

where $\tau = 1 - T/T_c$, $B = 235.8 \text{ mN} \cdot \text{m}^{-1}$, $b = -0.625$, and $\mu = 1.256$. Equation 1.15 gives a decrease of the surface tension as the temperature increases, declining

to zero at the critical point. The uncertainties associated with Eq. 1.15 are given in the IAPWS Release; they are on the order of 0.5% at low temperatures, increasing to 1% and beyond as the temperature approaches T_c . While Eq. 1.15 describes the surface tension between coexisting vapor and liquid water, it also describes well the surface tension of a water–air interface at low and moderate temperatures and pressures.

1.6.2. Dielectric Constant

The static dielectric constant, which describes the ability of a solvent to be polarized by an electric field, is commonly used in studies of solution chemistry. A higher dielectric constant is typically associated with a greater ability to dissolve electrolytes or polar compounds. Liquid water has a higher dielectric constant than most liquids because of its polarity and the association of molecules due to hydrogen bonds.

A standard formulation for the static dielectric constant of water has been developed by Fernández *et al.* (1997). Figure 1.9 shows values calculated from this formulation. The values for the vapor at 0.1 MPa are too close to unity to be visible on the graph. The dielectric constant of the liquid at room temperature is near 80 (with only a small dependence on pressure), but declines rapidly at higher

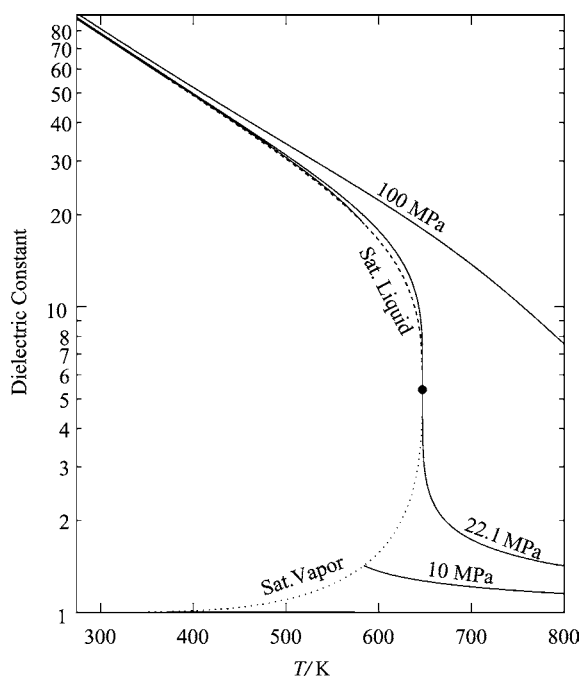


Fig. 1.9. Static dielectric constant of water.

temperatures as the density (and correspondingly the extent of hydrogen bonding) diminishes, reaching a value near five at the critical point.

The frequency-dependent dielectric behavior of water is of some interest; this is summarized in a review by Ellison *et al.* (1996). More details of dielectric relaxation in liquid water from 0 to 35 °C are given by Buchner *et al.* (1999).

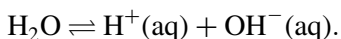
1.6.3. Refractive Index

The refractive index describes the interaction of a substance with electromagnetic radiation. It depends on frequency; visible and near-visible frequencies are most often studied. Water's refractive index in the visible region is not qualitatively different from other fluids, with values in the dense liquid near 1.3. A standard formulation exists (Harvey *et al.*, 1998) for the wavelength range between 0.2 and 1.1 μm , with good extrapolation behavior in the near infrared up to about 1.9 μm . At wavelengths further into the UV and IR, there are absorption features that complicate the refractive index behavior.

The frequency-dependent refractive index and absorption behavior of liquid water have also been extensively studied at ambient conditions throughout the infrared spectrum; this work is summarized by Bertie and Lan (1996).

1.6.4. Ionic Dissociation Constant

Water dissociates slightly into positive and negative ions; this equilibrium is important in the study of electrochemical reactions in water, especially those involving acids and/or bases (such equilibria are discussed extensively in Chapter 13). The reaction can be written as



When the activity of undissociated H_2O is taken as unity and the ion concentrations are measured in molality units, the equilibrium constant K_w of the reaction is approximately 10^{-14} for liquid water at ambient temperature, producing the familiar value of 7 for the pH of neutral water. The equilibrium concentrations vary with pressure and temperature; in general, higher temperatures favor dissociation, but lower densities strongly reduce the dissociation. As a result, K_w of the saturated liquid increases somewhat with temperature, but then decreases near the critical point as the density begins to be reduced more quickly. The dissociation in low-density steam is very small; K_w under these conditions is estimated to be on the order of 10^{-50} (Pitzer, 1982).

Marshall and Franck (1981) analyzed the data available to them and produced a representation for K_w as a function of temperature and density. Further examination (Pitzer, 1982) showed that this formulation did not exhibit the correct behavior at low densities, and IAPWS subsequently recommended that it

not be used for densities below $0.45 \text{ g}\cdot\text{cm}^{-3}$. Experimental determination and model representation of K_w at high temperatures and low densities are currently active areas of research (Bandura and Lvov, 2004).

1.7. Heavy Water

As mentioned before, ‘heavy water’ is defined to be the same as ordinary water except that the hydrogen consists entirely of the deuterium (relative mass 2) isotope. D_2O is of substantial scientific interest in the study of isotope effects, and also finds some industrial application. The properties of D_2O differ slightly from those of ordinary water, primarily due to stronger hydrogen bonding. D_2O freezes at a higher temperature than H_2O ; its triple-point temperature is approximately 276.97 K. The vapor pressure of D_2O is lower at temperatures up to approximately 494 K, after which it slightly exceeds that of H_2O . The critical properties of D_2O are given in Table 1.3.

The current standard formulation for the thermodynamic properties of D_2O is that of Hill *et al.* (1982). Formulations for its viscosity and thermal conductivity have been issued by IAPWS (1982), as has a formulation for its surface tension (IAPWS, 1994b). A correlation for the vapor pressure of heavy water from its triple point to its critical point has been given by Harvey and Lemmon (2002).

1.8. Water as a Solvent

Subsequent chapters will cover in detail the solubility in water of various classes of compounds; here we give a qualitative overview. Because of water’s polarity, it is a good solvent for polar substances, especially those (such as alcohols) that can form hydrogen bonds with water molecules. The polarity and high degree of association of liquid water produce a high dielectric constant; this lowers the energetic penalty for the formation of ions, making many salts soluble in water to a substantial extent. In contrast, nonpolar compounds are not easily incorporated into water’s structure, and therefore, tend to be nearly insoluble in water.

The effect of temperature on aqueous solubility is often not straightforward. An increase in temperature tends to drive volatile solutes out of solution, reducing their solubility. However, this can be compensated by water’s expansion with temperature, allowing more ‘room’ for the solute molecules. As a result, the aqueous solubilities of volatile solutes such as common gases (as discussed in Chapter 3) typically pass through a minimum with temperature. Because the degree of hydrogen bonding and the dielectric constant decrease at high temperatures, water behaves more like a nonpolar solvent (more able to dissolve nonpolar substances, less able to dissolve electrolytes) at those conditions.

Table 1.6. IAPWS Releases for properties of water and heavy water

Property	Date of latest version
Viscosity ^a	2003
Thermal conductivity ^a	1998
Refractive index	1997
Static dielectric constant	1997
Thermodynamic properties (industrial use) ^b	1997
Thermodynamic properties (general and scientific use)	1996
Surface tension	1994
Surface tension (D ₂ O)	1994
Melting and sublimation pressures	1993
Saturation properties (Supplementary Release)	1992
Critical point properties	1992
Thermodynamic properties (D ₂ O)	1984
Viscosity and thermal conductivity (D ₂ O)	1984
Ion product	1980

IAPWS Releases may be downloaded from www.iapws.org.

^aThis Release contains formulations both for industrial use and for general and scientific use.

^bThis Release has been supplemented in 2001 by a Supplementary Release on backward equations for calculating $p(h, s)$ and in 2003 by a Supplementary Release on additional backward equations.

1.9. Where to Get More Information

Standards for water properties are set by IAPWS, which issues ‘Releases’ that describe specific well-studied properties with the best accuracy and precision available. It also issues ‘Guidelines’ for properties, including selected properties of key aqueous mixtures, in cases where the information is more uncertain and may need to be revised when new data become available. Tables 1.6 and 1.7, respectively, list the currently available IAPWS Releases and Guidelines.

Table 1.7. IAPWS Guidelines for properties of water and aqueous solutions

Property	Date of latest version
Thermodynamic properties of ammonia–water mixtures	2001
Critical locus of aqueous solutions of sodium chloride	2000
Distribution of gaseous solutes between steam and water	1998
Solubility of sodium sulfate in aqueous mixtures of sodium chloride and sulfuric acid	1994
Solubilities of simple apolar gases in light and heavy water at high temperature	1993
Electrolytic conductivity of water	1990

IAPWS Guidelines may be downloaded from www.iapws.org.

IAPWS Releases and Guidelines may be downloaded from the IAPWS Website at <http://www.iapws.org>. They are also reprinted in the Proceedings volumes of the International Conferences on the Properties of Water and Steam, held every 5 years (White *et al.*, 1995; Tremaine *et al.*, 2000). Finally, paper copies may be ordered from the Executive Secretary of IAPWS: Dr. R.B. Dooley, EPRI, 3412 Hillview Ave., Palo Alto, CA 94304, USA.

For more comprehensive scientific information about many aspects of water, we direct the reader to a seven-volume treatise (Franks, 1972–1982) that contains contributions from many leading practitioners in the study of water and aqueous solutions. The chapter by Tödheide (1972) on water at high temperatures and pressures is particularly relevant. A more popular account of water in all its forms and functions is given by Ball (2000).

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