Supercritical Water as a Solvent
Hermann Weingärtner* and Ernst Ulrich Franck

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1. Introduction

Water, in many respects, shows unique properties that are well characterized at ordinary conditions. Water can also exist, and has been investigated, at states far above its critical temperature of 647 K, where it can be gradually compressed from gas-like to liquid-like densities. The resulting dense supercritical states possess remarkable properties which differ largely from those at normal conditions.\(^{[1,3,4]}\) Adopting a term from geochemistry, such supercritical, aqueous systems are often denoted as hydrothermal fluids.

Investigations of density variations are the key to understanding fluid behavior because such experiments allow the temperature dependence of the fluid properties to be separated from their volume dependence.\(^{[2]}\) To achieve substantial density variations, pressures up to several hundred MPa are required. For example, for water at 773 K, a pressure of 1 GPa is needed to generate the ordinary liquid density of 1 g cm\(^{-3}\). Under such conditions it is likely that water will corrode the vessels. Experiments must therefore contend with conditions of high temperature, high pressure, and high water corrosivity.

Under the conditions of interest, the molecular and electronic structures of most substances are not appreciably deformed, however, hydrogen bonds are highly sensitive to temperature and pressure. For example, the increase in the electrical conductance of fluid water at high temperatures and pressures indicates a transition from molecular to ionic electrical conductance of fluid water at high temperatures and form, and the basis for innovative technologies. This Review covers the current knowledge of the major properties of supercritical water and its solutions with nonpolar, polar, and ionic compounds, and of the underlying molecular processes.

miscible with nonpolar compounds, while polar and ionic compounds remain highly soluble as well. In addition, the viscosity remains low, even at liquid-like densities, which enhances mass transfer and diffusion-controlled chemical reactions. There are many interesting reactions, such as the oxidation, pyrolysis, and hydrolysis of organic compounds, where supercritical water acts as a solvent or reactant or catalyst.\(^{[7]}\)

Perhaps the most fascinating application is the destructive oxidation of organic waste in the supercritical water oxidation (SCWO) process.\(^{[8]}\) At some conditions, organic waste, for example polychlorinated biphenyl compounds, is highly miscible with water. In the presence of oxygen, such compounds react to carbon dioxide, water, and some other small molecules. By careful choice of temperature and pressure, partial oxidation of organic molecules, for example of methane to methanol, can be achieved as well.\(^{[9]}\) Because the dielectric constant increases with water density, high pressure favors the formation of polar over nonpolar oxidation products.

A phenomenon with considerable prospects is the production of combustion flames in a supercritical environment. Figure 1 shows a “hydrothermal” flame burning in a homogenous mixture of water and methane to which oxygen is injected from a nozzle.\(^{[8a]}\) In this aqueous environment, spontaneous flame ignition occurs at 673 K, markedly below that of gaseous oxygen and methane mixtures. Such flames can burn for 30 min or even longer, and have been spectroscopically investigated\(^{[10]}\) and modeled.\(^{[11]}\)

Another field of major interest is geochemistry,\(^{[12,13]}\) where supercritical water acts as a solvent for hydrothermal reactions, such as mineral formation, deposition, or disolu-

\(^{[4]}\) Prof. Dr. H. Weingärtner
Physikalische Chemie II
Ruhr-Universität Bochum
44780 Bochum (Germany)
Fax: (+49) 234-321-4293
E-mail: hermann.weingaertner@ruhr-uni-bochum.de

\(^{[5]}\) Prof. Dr. Dr. h.c. E. U. Franck
Institut für Physikalische Chemie
Universität Karlsruhe
76128 Karlsruhe (Germany)

\(^{[6]}\) Deceased
tion in the Earth’s mantle. Water also participates in the formation of methane and heavier hydrocarbons of natural petroleum. Pressure increases in the Earth’s mantle by about 1 GPa for every 30 km of depth, so geothermal brines typically have pressures above 100 MPa and temperatures above 500 K. Water at even more extreme conditions is present in the outer planets Neptune and Uranus, which contain a thick layer of “hot ices” between the outer atmosphere and the core. In the laboratory, such conditions were mimicked in shock waves to pressures 180 GPa and 10000 K, where the water density is 4 g cm$^{-3}$, that is, four times the normal liquid density.

In recent years, there has been great progress in the characterization of the properties of supercritical water and aqueous solutions, and the number of applications has rapidly increased. New experimental techniques now push the limits to extreme conditions of temperature and pressure, increase the experimental accuracy, and provide access to bulk and molecular properties previously not available. Theory and computer simulations greatly improve the understanding of these properties at the molecular level.

This Review covers these developments which are at the root of modern supercritical water technologies. To keep the Review manageable, we primarily focus on dense states with high solute concentrations, such as encountered in many chemical reactions in nature, the laboratory, and applications. In the literature, the main emphasis is on dilute aqueous solutions at moderate densities around 0.3 g cm$^{-3}$ which is near the critical point of pure water. The solvent properties of dense supercritical water were first reviewed in 1961, when the field was in its very infancy. The latter review may be consulted for the historical background.

2. Supercritical Water

2.1. Phase Diagram

Figure 2 shows the phase diagram of water in the temperature-density ($T_\rho$) plane. Isobars indicate the pressures. At

Figure 1. “Hydrothermal” flame, burning in a homogeneous supercritical aqueous mixture of 70 mol% water and 30 mol% methane at 100 MPa pressure and 713 K environmental temperature, observed through the sapphire windows of a high-pressure vessel. Oxygen is injected from below through a nozzle at a rate of 3 mm$^3$ s$^{-1}$. The height of the flame is about 3 mm. The “gas funnel” around and above the flame shows the upward flow of reaction products at higher temperatures and lower density, which generate a Schlieren contrast. There is no phase separation.

Ernst Ulrich Franck was born in 1920 in Hamburg. He received his doctoral degree in 1950 for work performed in the group of A. Eucken in Göttingen about transport phenomena in gases. Initiated by this work, and in contact with mineralogists at the University of Göttingen, above all with C. W. Correns, he established his research subject, the study of supercritical fluids. After his “Habilitation” in 1956 he spent a research fellowship at Oak Ridge. In 1961 he was appointed to the chair of Physical Chemistry at the University of Karlsruhe, where he stayed until his retirement in 1988, interrupted by many visiting fellowships. He received many scientific awards and was a member of several scientific academies. Ernst Ulrich Franck died on December 21, 2004, an obituary was published in ref [121].

Hermann Weingärtner was born in 1948 in Offenburg. He received his doctorate in 1976 for work carried out in the group of H. G. Hertz in Karlsruhe on nuclear magnetic resonance in electrolyte solutions. After his “Habilitation” in 1986 and after several research fellowships, among others at the Australian National University in Canberra, he was appointed, in 1995, to a professorship in Physical Chemistry at the Ruhr-University of Bochum. His major scientific activities are in the field of thermophysical properties and phase transitions of fluids.

Figure 2. Temperature-density diagram of water with isobars. Solid circles mark breaks in the melting line which arise from phase transitions between the ice polymorphs. TP indicates the S–L–G triple point at 273.15 K. CP indicates the L–G critical point.
298 K, liquid water with a density of 0.997 g cm\(^{-3}\) coexists with water vapor with a density of 2 \times 10^{-5} g cm\(^{-3}\). With increasing temperature, the density of the liquid decreases and that of the vapor increases. At the critical point both phases become identical and the dividing meniscus disappears. The critical temperature \((T_c)\), pressure \((P_c)\), and density \((\rho_c)\) are: \(T_c = 647.1\ \text{K},\ P_c = 22.1\ \text{MPa},\ \rho_c = 0.322\ \text{g cm}^{-3}\). Applications typically use range from the critical density to liquid-like densities of about 1 g cm\(^{-3}\).

The fluid range is encompassed by the melting line. Breaks in the melting line indicate transitions between several solid polymorphs of ice. Starting from the solid–liquid–gas (S–L–G) triple point at 273.15 K, where conventional ice I\(_s\) is stable, the melting line initially decreases (S, L, and G denote the solid, liquid, and gaseous phases, respectively). At 251 K and 220 MPa a new phase of ice (ice III) occurs, and the melting line turns to higher temperatures. There follow other polymorphs, the ices IV, V, and VI, until at 354.8 K and 2.17 GPa ice VII is formed. Ice VII is the only experimentally observed polymorph at equilibrium with supercritical water.

The observation of such high-pressure, high-temperature phase transitions is highly difficult. Great experimental progress has been achieved by the development of diamond anvil cells\(^{[17]}\). As schematically sketched in Figure 3, a small amount of sample is held in a metal gasket between the flat-polished opposite faces of two diamonds.

The regime between the static and dynamic data, typically beyond 20 GPa and 4500 K, is of great interest in the geochemical sciences, but extrapolations are speculative because new solid phases (ice modifications) might occur. To some extent, experimentally inaccessible states of water can be explored by molecular dynamics (MD) simulations, in particular, if quantum-mechanical (ab initio) approaches are used. Ab initio MD simulations\(^{[20]}\) indeed predict a further solid polymorph at coexistence with fluid water. In this “superionic” phase the proton jumps between the two equivalent positions along the O–O axis. By such simulations, the melting line was considered up to conditions in the interior of Neptune, and suggested that regime of “hot ices” in Neptune’s interior is fluid rather than solid\(^{[21]}\).

2.2. \(P,V,T\) Behavior

Accurate pressure \((P)\), volume \((V)\), and temperature \((T)\) data are not only of interest in itself, but also form a prerequisite for other studies because experiments are usually performed at given pressure and temperature, while they are easier understood as a function of volume and temperature. At moderate pressure, \(P,V,T\) data can be measured by static experiments, in which water is introduced into a pressure vessel, and the volume of water is determined at given temperature and pressure. Many years ago, Burnham et al.\(^{[22]}\) and Franck and co-workers\(^{[23]}\) pushed such experiments to 1273 K and 1 GPa, which forms the experimental limit of such techniques. It is believed that the uncertainties in the density values measured does not exceed 0.5 %, but as \(P,V,T\) data enter into many analyses of other data, such a high accuracy is mandatory.

\(P,V,T\) data beyond these limits were derived from dynamic experiments using shock-wave techniques. Denoting the state prior to release of the shock wave by index “0”, shocked states obey the Hugoniott relation for the internal energy \(U\) [Eq. (1)].

\[
U-U_0 = (P-P_0)(V-V_0)/2
\]  

Thermodynamic assumptions can be used to transcribe the measured \(U,P,V\) data into \(P,V,T\) data. More accurate temperature measurements can be made from the emission spectrum of the probe as determined by pyrometry. In this way, Nellis and co-workers determined \(P,V,T\) data up to 80 GPa and 5200 K.\(^{[24]}\)

The regime between the static and dynamic data, typically between 1 and 10 GPa, is of great interest in geochemistry. Efforts are currently being made to bridge this gap by new experimental techniques. Diamond anvil cells are suited to generate these pressures, but do not provide direct volume information. Recently, \(P,V,T\) data up to 5 GPa and 673 K\(^{[25]}\) could, however, be deduced indirectly from measurements of the speed of sound. Another remarkable method uses synthetic fluid inclusions, which are hydrothermally generated in heating fractures of quartz or corundum. After quenching to low temperature, the inclusions retain the properties of the fluid before trapping. By this technique,
2.3. Equations of State

The \(PVT\) surface of fluids is usually described by a pressure-explicit thermal equation of state \(P(V,T)\). An appropriate theory would predict phase equilibria, \(PVT\) behavior, and other thermodynamic properties in the homogenous regime from a few physically significant input parameters. At present, no molecular-based equation of state fits these criteria.

In principle, simulations by Monte Carlo (MC) and molecular dynamics (MD) techniques can provide molecular-based equations of state, but are not yet accurate enough for applications. Moreover, there are considerable difficulties in simulations of supercritical water, because the success of simulations largely relies on the knowledge the intermolecular interaction potentials. For water, a large number of model potentials have been suggested and parameterized with regard to properties at ordinary conditions. The parameterization depends however on temperature and pressure, and the experience gained at ordinary conditions cannot easily be transferred to supercritical states. Moreover, in some cases, the subtleties of hydrogen-bonding may require ab initio MD simulations.

Formulations of \(PVT\) behavior suited for applications rely on empirical or semi-empirical approaches, often with a large number of regressed parameters. The very properties that make supercritical fluids so useful, that is, the transition from gas-like to liquid-like behavior, render modeling efforts to be difficult. Because of their simplicity many workers prefer semi-empirical, “cubic” equations, which usually form the basis for molecular dynamics (MD) simulations. In addition, such cubic equations usually involve parameters of some physical significance, which facilitates data extrapolations. Many equations along these lines have been proposed for fluids in general, but are often difficult to apply for supercritical water. For example, at very high pressures water remains much more compressible than can be captured by the typical repulsive interaction potentials. For water, a large number of regressed parameters. The very properties

Equations of State

There remain discrepancies among these various data sets, so that the \(PVT\) relation above 1 GPa is still uncertain.

2.4. Critical Anomalies

Near liquid–gas (L–G) critical points some properties show divergences which obey asymptotic scaling laws of the form of Equation (2) where \(\tau = \left( \frac{T - T_c}{T_c} \right)\) defines the temperature difference from the critical point, \(X_0\) is a system-specific amplitude, and \(\mu\) is a universal critical exponent.

\[
X = X_0 \tau^\mu + \ldots \quad \text{as} \quad T \to T_c
\]

Analytical equations of state can be expanded in a Taylor series everywhere, including the critical point, and by such expansions at the critical point the critical exponents of the various properties \(X\) turn out to be integers or rational fractions. For example, the L–G coexistence curve in Figure 2 obeys a scaling law of the form of Equation (3) where the so-called order parameter \(\Delta P\) is given by the difference of the densities of the liquid \((\rho_L)\) and gaseous \((\rho_g)\) phases. Any analytical equation of state provides an exponent \(\beta = 1/2\), which implies a parabolic coexistence curve.

\[
\Delta P = \rho_L - \rho_g = B_1 \tau^\beta + \ldots
\]

Analytical theories are denoted as “classical” or “mean-field” equations. The term “mean-field” accounts for the fact that, in molecular theories, analytical expressions are obtained by assuming that the interaction of a particle with its neighbors can be represented by the mean field generated by its neighbors.

Experiments, however, provide critical exponents that do not conform to the mean-field values, they give irrational exponents and have a non-analytical behavior. Instead, the critical behavior of the L–G transition can be described by the three-dimensional Ising spin 1/2 model. This model was originally developed for describing the interactions of spins leading to ferromagnetic transitions. It considers the nearest neighbors of a particle only and presumes short-range interactions, typically with a \(r^{-6}\) separation dependence. Renormalization group theory allows the exact values for critical exponents to be computed. The predicted value of the Ising exponent, \(\beta = 0.326\ldots\), is confirmed by accurate data for L–G transitions in fluids. Among other things, this behavior implies that near the L–G critical point the coexistence curve in Figure 2 is approximately cubic, and much flatter than the parabolic shape predicted by analytical theories.

In the mean time, there is a widespread recognition that these anomalies give rise to considerable deficits in the traditional equations of state. In the best case the anomalies occur only close to \(T_c\). These “weak anomalies” are indeed of little significance in chemical processes, and it is not crucial.
for applications to use a physically correct representation of the critical divergences. In the worst case the non-classical behavior extends over a wide temperature range. A prominent example for such a “strong anomaly” is the isobaric heat capacity \( C_P \) which goes to infinity at the critical point. About 30 K above \( T_c \), the isothermal density dependence of \( C_P \) still shows a very pronounced maximum with a \( C_P \) value that is by an order of magnitude larger than that extrapolated from data taken far away from the critical point.\(^{[16,19]}\) Even fully empirical equations, such as the IAPWS-95 equation mentioned earlier\(^{[20]}\) include some non-analytical terms to obtain accurate descriptions of this behavior. In applications, the regime of large variations is difficult to control, and is usually avoided.

From the theoretical perspective, the anomalous phenomena close to \( T_c \) are now well understood. Large difficulties arise, however, from the need to account for the transition from asymptotic Ising-like behavior near critical points to mean-field behavior expected to prevail far away. This crossover forms the major reason for the large number of adjustable terms needed in accurate equations of state of the traditional form.\(^{[23]}\) The need for a proper description of crossover has given rise to intense experimental and theoretical efforts. Sophisticated parametric crossover theories for fluids are now available\(^{[32]}\) and have been applied to water.\(^{[34]}\) “Parametric” means that a physically plausible crossover function with a few adjustable parameters is used to interpolate between the mean-field and Ising limits. In comparison with fully empirical approaches with a large number of parameters, crossover theories are of similar precision, but are more difficult to implement and require more computer time. It is likely that the future increase in computer power will, however, favor crossover theories also with regard to applications.

2.5. Autodissociation

A key property in many applications is the dissociation equilibrium \( \text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{OH}^- \), which is characterized by the equilibrium constant \( K \) [Eq. (4)] or the ion product \( K_w \) [Eq. (5)], where \( a \) refers to the activities of the species. At normal conditions, ion concentrations are sufficiently low to replace the activities by concentrations. Equations (4) and (5) are usually formulated with \( \text{H}_2\text{O}^+ \) rather than \( \text{H}^+ \), but at supercritical states such a formulation is by no means straightforward.

\[
K = \frac{a(\text{H}^+)a(\text{OH}^-)}{a(\text{H}_2\text{O})} \quad (4)
\]

\[
K_w = a(\text{H}^+)a(\text{OH}^-) \quad (5)
\]

Because charged species are involved, the ion product can be studied by electrochemical methods, such as electrical conductance measurements. More than thirty years ago, Holzapfel and Franck\(^{[35]}\) performed such measurements to 1273 K and 1 GPa. Later, shock-wave experiments pushed this limit to 180 GPa and 10000 K.\(^{[35]}\) Figure 4 shows the temperature- and density-dependence of the ion product, derived from the ion product tables of Marshall and Franck.\(^{[35]}\) At normal conditions, \( K_w = 1 \times 10^{-14} \) and the proton concentration possesses the familiar value of \( 1 \times 10^{-7} \text{ mol L}^{-1} \). \( K_w \) increases with temperature and density. At 1273 K and liquid-like density, \( K_w \) is at least six orders of magnitude larger than at 298 K. This situation has dramatic consequences for hydrolysis and acid–base equilibria. For example, at 773 K and 200 MPa the equilibrium constant of the hydrolysis reaction \( \text{Cl}^- + \text{H}_2\text{O} \leftrightarrow \text{HCl} + \text{OH}^- \) is by about nine orders of magnitude larger than at normal conditions, and the hydrolysis of alkali halides is comparable to that of acetates at normal conditions. Thus, corrosion will be greatly enhanced.

The increase in ionization is corroborated by recent shock-wave experiments to 180 GPa and 10000 K.\(^{[35]}\) Near 1000 K and densities of about 2 g cm\(^{-3}\) the conductivity begins to level off a value of about 30 S cm\(^{-1}\), which is comparable to that of molten hydroxides. Raman spectra of shock-compressed water indeed show the stretch vibration of the \( \text{OH}^- \) ion, but remarkably, no band for \( \text{H}_2\text{O}^+ \) is found.\(^{[35]}\) The lack of a \( \text{H}_2\text{O}^+ \) band gives rise to the suspicion that the cation is \( \text{H}^+ \).\(^{[36]}\) It has been noted\(^{[37]}\) that these highly conducting states are of relevance for the interpretation of the large magnetic fields of the outer planets. At the high-temperature end of the shock-wave experiments, one may even be close to metalization of water, although no evidence for electronic contributions to the conductance was found.\(^{[38]}\) Ab initio MD simulations locate the closure of the band gap at 7000 K near 300 GPa inside the fluid region.\(^{[23]}\)

2.6. Transport Coefficients

Because all transport coefficients strongly depend on the viscosity of the medium, an accurate knowledge of the viscosity of supercritical water is mandatory. Figure 5 shows experimental data for the viscosity, \( \eta \), to 823 K and 350 MPa.\(^{[38]}\) The diagram is supplemented by low-pressure data\(^{[39]}\) and by plausible extrapolations to 1273 K. Projected on the floor of the cube is the liquid–gas coexistence curve which indicates the two-phase regime.
The mutual diffusion coefficient, \( D \), differs drastically from the diffusion–viscosity relation, which differs markedly at liquid-like densities. The low-density behavior reflects translational momentum transfer and is well described by the kinetic theory of gases. In the high-density regime collisional momentum transfer prevails, which is not yet understood in detail. There is a wide range of densities, between 0.6 and 0.9 g cm\(^{-3}\), where \( \eta \) depends only weakly on temperature and density. In this range, \( \eta \) amounts only to about one tenth of its value at normal conditions. This high fluidity is attractive in chemical processes because mass transfer and diffusion-controlled chemical reactions are largely enhanced.

The low viscosity reflects high molecular mobilities. The mean-square displacement \( <r^2>\) of a particle during time \( t \) is described by the self-diffusion coefficient \( D = <r^2>/6t \). At normal conditions \( D \approx 2.3 \times 10^{-9} \text{ m}^2/\text{s} \), at 973 K and liquid-like density \( D \approx 10^{-8} \text{ m}^2/\text{s}^1 \). A similar enhancement of molecular motions is found by nuclear magnetic [40] and dielectric [41] relaxation techniques which probe molecular rotations. Correspondingly, the thermal conductivity is high [39,42] and thus exothermal chemical reactions can be controlled more easily.

In dense states a hydrodynamic approach is known to work quite well. Thus, the self-diffusion coefficient of a particle of effective radius \( r \) obeys the Stokes–Einstein relation [Eq. (6) where \( k_B \) is the Boltzmann constant].

\[
D = \frac{k_B T}{6\pi ho r}
\]  

Equation (6) does not only apply to self-diffusion of water, but also to the diffusion of traces of solutes in water. At decreasing water density, Equation (6) holds at least down to the critical density. [39] Thus, over a large range of conditions the factor \( D \eta / T \) is almost constant, which facilitates prediction of solute diffusion. In the dilute gas limit, \( D \) is proportional to the ratio \( \eta / \rho \) of the viscosity and density, which differs drastically from the diffusion–viscosity relationship in dense phases.

In applications, mutual diffusion, often simply termed “diffusion”, is of far greater importance than self diffusion. The mutual diffusion coefficient, \( D_{12} \), describes mass flows driven by gradients in concentrations in mixtures, as described by Fick’s laws. At the critical point, \( D_{12} \) goes to zero, which is known as “critical slowing-down”. In the only study of mutual diffusion for supercritical aqueous mixtures so far conducted, Buelow and co-workers have demonstrated that critical slowing-down in concentrated solutions of NaNO\(_3\) exceeds over a comparatively wide region. [43] Thus, diffusion-controlled reactions in concentrated solutions may be markedly slower than usually presumed. It can, however, be rigorously shown that critical slowing-down must disappear at infinite dilution of the solute. Therefore, in dilute solutions this phenomenon can probably be ignored.

### 2.7. Dielectric Properties

The relative dielectric permittivity (“dielectric constant”), \( \varepsilon \), of water controls the solvent behavior and the ionic dissociation of salts. Accurate experimental data for \( \varepsilon \) over large regions of temperature and pressure are therefore necessary for many applications. Figure 6 shows the dielectric constant to 1273 K and 1 g cm\(^{-3}\), based on experimental data to 823 K and 500 MPa [44] and model calculations for higher temperatures [45]. \( \varepsilon \) decreases with increasing temperature and increases with increasing density. The familiar high value of \( \varepsilon \approx 80 \) occurs only in a small region at low temperatures. In a large supercritical region at high densities, the dielectric constant has values of the order of \( \varepsilon = 10–25 \). These values are similar to those of dipolar liquids, such as acetonitrile or...
acetone under ordinary conditions. These values are sufficiently high to dissolve and ionize electrolytes, but also enable miscibility with nonpolar solutes. At low densities the dielectric constant, and thus the ability to dissolve and ionize electrolytes, decreases rapidly. At the critical point \( \varepsilon = 6.3 \).\[44\]

The high values of \( \varepsilon \) at normal conditions result from preferred dipole orientations in the water structure. In molecular theory, non-random dipole orientations are described by the Kirkwood factor \( g_K \), which in modern formulation is related to \( \varepsilon \) by Equation (7),\[46\] where \( N/V \) is the number density of the dipoles, \( \mu \) the dipole moment of the isolated molecule, \( \varepsilon_\infty \) the high-frequency limit as a result of nuclear and electronic displacement polarizations, \( \varepsilon_0 \) is the permittivity of free space; \( g_K \)-values different from unity indicate preferred parallel (\( g_K > 1 \)) or antiparallel (\( g_K < 1 \)) dipole orientations.

\[
\frac{(\varepsilon - \varepsilon_\infty)(2 \varepsilon + \varepsilon_\infty)}{\varepsilon_\infty(2 + \varepsilon_\infty)^2} \cdot \frac{\mu^2 g_K}{9 \varepsilon_0 kT} \left( \frac{N}{V} \right)
\]

(7)

With regard to applications there is need for an accurate formulation that represents the dielectric constant over wide ranges of temperature and pressure,\[47\] which should be suitable for some extrapolation beyond the underlying range of experimental data. It has long been suggested that models for the Kirkwood factor may be simpler than for the dielectric constant itself.\[48\] Irrespective of the well-defined molecular meaning of \( g_K \), all accurate data correlations of \( \varepsilon \) over wide ranges of pressure and temperature are, however, empirical. Some frequently used data correlations result, however, in quite different high-temperature and high-pressure extrapolations.\[49\] Because at high temperatures water looses its peculiarities, it may be more fruitful to exploit some solvable models of statistical mechanics as a guide for extrapolation. An attempt based on expressions for dipolar hard spheres seems promising.\[50\]

From the scientific perspective, the Kirkwood factor and the dielectric constant form useful targets for testing theories and simulations. Moreover, \( g_K \) may form a global measure of the water structure.\[51\] A physically significant computation of \( g_K \) through Equation (7), however, is a subtle problem.\[52\] Moreover, ab initio simulations suggest that the electric field induced by surrounding particles enhances the dipole moment of a hydrogen-bonded molecule, so that \( \mu \) increases from the dilute gas to dense water.\[53\]

### 2.8. Hydrogen Bonding and Water Structure

At ordinary conditions the structure of water is dominated by a three-dimensional network of hydrogen bonds. It is a central question of any molecular approach to what extent these hydrogen-bonded structural patterns survive in the supercritical fluid. At the very outset, any such discussion requires a criterion for deciding when two neighboring molecules can be described as being hydrogen bonded. In simulations, hydrogen bonds are usually defined by energetic or structural properties of the molecular pair. Experimentists resort to operational definitions, such as frequency shifts in spectra. The various criteria can lead to largely different estimates of the number of hydrogen bonds.\[54\]

In vibrational spectroscopy, hydrogen bonding leads to frequency shifts, changes in band contours, and the appearance of new bands. Infrared spectra to 823 K and 400 MPa were reported more than thirty years ago,\[55\] and were later supplemented by Raman data.\[56\] Figure 7 shows Raman spectra of the O–D symmetric stretch vibration of a solution of 5 mol% D₂O in H₂O.\[57\] Spectra coincide. The possible hydrogen-bonded states give rise to complex multimodal spectra with overlapping component bands. Thus, spectral analyses is usually based on models. A major feature observed in going at liquid-like density from 298 K to 673 K, is that the band at 2450 cm⁻¹ is gradually replaced by a band at 2650 cm⁻¹. If at 673 K the density is lowered, the band at 2650 cm⁻¹ shifts to higher frequencies and approaches the limiting frequency of 2727 cm⁻¹ of the highly dilute gas. Irrespective of details of data evaluation, it is clear that in dense supercritical water, at least at the temperatures considered, hydrogen bonding is retained to an appreciable extent.

Another long established measure of hydrogen bonding is the chemical shift of the OH proton in the ¹H NMR spectrum, but only in 1997 were such data reported for supercritical water.\[58\] In contrast to vibrational spectroscopy, the longer time scale of the NMR experiments only provides an average degree of hydrogen bonding over the various configurations. The results of NMR and vibrational spectroscopy are consistent with one another.

Information on the water structure, and thus on hydrogen bonding, is also expected from scattering techniques. Neutron scattering is particularly suitable because, by using isotopically substituted samples, the distribution function of the intermolecular oxygen–hydrogen separation can be extracted.
Difficult corrections and sophisticated numerical procedures are, however, required to evaluate the O–H-separation distribution functions from the raw scattering patterns. Thus, the interpretation of neutron scattering results for supercritical water has been controversial. A detailed discussion is given in a review by Chialvo and Cummings.[27] Herein we note only that, in contrast to earlier claims,[35] neutron scattering confirms the presence of hydrogen-bonded configurations in dense supercritical states.[56] While the experimental knowledge of the detailed water structure in the supercritical region is still far from being complete, the interplay between experiment and simulation has now singled out the major structural motifs.[27]

In summary, there is no doubt that hydrogen bonds are still present in dense supercritical water. This situation clearly reflects the fact that at the critical temperature the energy of the hydrogen-bond is still markedly larger than the thermal energy. The hydrogen-bonded configurations probably consists of dimers and small clusters.[27] The properties of water clusters are theoretically understood in great detail.[57] The extended network structure that is responsible for the unique properties of liquid water is, however, lost. It remains to exploit this knowledge in terms of models for thermophysical properties.

3. Aqueous Mixtures with Nonpolar Compounds

3.1. General Topologies of Phase Diagrams

As a rule of thumb, water is a good solvent for electrolytes and hydrophilic substances, while it shows low solubilities for nonpolar substances. This behavior depends, however, on temperature and pressure. In the supercritical regime the solubility can be tuned by density, and thus by pressure, which opens many possibilities for using supercritical water as a solvent and reaction medium.

When a solute is added to water, the L–G critical point is displaced, giving rise to a locus of L–G critical points, the so-called critical curve. In addition, liquid–liquid (L–L) phase equilibria may occur and interfere with the L–G critical regime. For a full description of this broad variety of phase behavior a three-dimensional pressure–temperature–mole-fraction ($P,T,x$) diagram must be used. The composition is, for example, given in terms of the mole fraction $x$ of one of the components. Often one resorts, however, to the projection of this diagram onto the $P,T$ plane. A theory of Konynenburg and Scott[58] suggests six types of phase diagrams in the $P,T$ projection. Albeit derived from an analysis of the simple van der Waals equation for mixtures, this topological scheme can also be applied to phase transitions in aqueous systems.[59] Three types of phase diagram of particular interest for supercritical aqueous solutions are depicted in Figure 8.

In the simplest cases, liquid–liquid immiscibility does not exist or does not extend into the gas–liquid critical region. In this sort of system, the vapor-pressure curves of the pure liquids are terminated by L–G critical points, which are connected by a continuous L–G critical curve for the mixtures. If the components are completely miscible at all conditions then the phase diagram is of type I shown in Figure 8. This type of behavior occurs for component molecules of similar shape and polarity. Examples are aqueous solutions of ammonia[60] and polar organic solutes, such as ethanol or acetone.[61]

For larger dissimilarities of the components L–L equilibria develop. These miscibility gaps are well-known phenomena in aqueous solutions of organic solutes. They result primarily from the hydrophobic nature of the solutes, which renders mixing with water entropically unfavorable. Schneider and collaborators have studied many L–L immiscibilities and their interference with L–G transitions,[62] recently also in diamond anvil cells to 2 GPa or higher.[63] For moderate hydrophobicity of the solute, the miscibility gaps are limited to low temperatures. In this case, the phase diagram has to account for the resulting L–L–G three-phase line, along which two liquid phases and the gaseous phase are in equilibrium. Additionally, there are one or more critical curves that describe the pressure dependence of the upper and/or lower temperatures of L–L demixing. In Figure 8 this behavior is exemplified for a so-called type II system. Actually, the possible phase behavior is much richer than shown.[59,62]

Most systems have, however, a disrupted critical curve. This interruption is crucial for understanding solubilities in supercritical water. In the following we presume that water is the less-volatile component of the binary mixture, as for example, encountered with inorganic gases and simple hydrocarbons. Then, in Figure 8 the water critical point is that at high pressure and high temperature. The reverse case, when water is the more-volatile component, for example, in mixtures with salts or minerals, will be discussed in Section 4.1.

Critical-curve interruption results from the fact that an increasing dissimilarity of the components displaces the L–L
equilibria to higher temperatures. Eventually, the L–L–G three-phase line merges into the L–G critical line, and the type II phase diagram is transferred into other types, of which only type III behavior in Figure 8 is of relevance here. Aqueous mixtures with nonpolar inorganic gases and simple hydrocarbons are important examples of type III systems.

In the type III phase diagram, a L–G critical curve starts from the critical point of the volatile nonpolar component. Because of the low solubility of water in nonpolar fluids at low pressure, this branch of the critical curve is, however, rapidly interrupted by the L–L–G three-phase line at a so-called critical end point. This regime of traces of water in the nonpolar fluid at low pressures is scarcely of interest for applications. Rather, we focus on the high-pressure branch of the critical curve, whose origin is in the critical point of water. This branch runs either directly to higher temperatures and pressures, or more often, it moves initially towards lower temperatures and then passes a minimum. In both cases, phase separations occur in some regions even above the critical temperature of pure water. Because above the critical temperature, the fluid is loosely denoted as a gas, this behavior is sometimes denoted as “gas–gas (G–G) equilibrium”. This notion is somewhat misleading because the coexisting phases possess liquid-like densities.

Figure 9 shows a section of the $PT_x$ diagram for type III systems near the critical point of water, and includes isobars and isotherms. The shaded regime indicates the two-phase regions of isobaric segments. The heterogeneous regime rapidly broadens at lower temperatures, so that eventually, nonpolar solutes are soluble in water only in trace amounts, and vice versa. The critical curve connects the maxima of the isotherms and the isobars forming a border, to the high-temperature side of which, is a region of complete miscibility.

3.2. Solubility of Nonpolar Solutes

The solubility of nonpolar, nonreacting inorganic and organic gases in water has often been studied by so-called synthetic or analytical techniques. In synthetic experiments, a mixture of known composition is introduced into the autoclave, and temperature and pressure are varied systematically. In simple cases the phase transition is observed visually. More generally, it manifests itself, for example, in breaks in $PT$ curves. The synthetic method gives not only $PT_x$ data, but can also be used to obtain volumetric data in the homogeneous regime, thus providing the equation of state. In the analytical method, samples of the coexisting phases are extracted from the autoclave and their composition is analyzed. The analytical method is particularly useful in the range of low gas concentrations, but gives no volumetric data.

A variety of autoclaves have been devised for recording high-pressure, high-temperature phase equilibria. Figure 10 shows an autoclave that enables both synthetic and analytical experiments. The cylindrical autoclave (A) is made from a corrosion-resistant nickel alloy. On both ends, windows of synthetic sapphires are mounted, which enable observation of the interior. On the outside there are several independent heat jackets (H) controlled by three thermocouples (T). Samples can be drawn through the connection (C) with a stainless steel capillary (SC) and a micrometric needle valve (not shown). The same connection (C) is used for filling, pressure transduction, and pressure measurement. The sample is magnetically stirred (not shown).

Figure 11 shows experimental critical curves for aqueous solutions of representative nonpolar inorganic and organic solutes. The hatched lines indicate the side where the systems form two phases. At the high-temperature side the compounds are completely miscible. It is likely that these curves are terminated at very high pressures by solid–fluid equilibria. There is manifold interest in these critical curves in diverse field of applications. From the industrial perspective, such curves are of key importance as border lines, beyond which chemical reactions can be conducted in homogeneous phases with high concentrations of the reactants. The miscibility with...
solutes such as methane or carbon dioxide is of great importance in geochemistry.

With increasing attractive interactions between the components, the shapes of the critical curves change in a regular fashion. For the small, hard solute helium the critical curve begins from the critical point of pure water with a positive slope. Hydrogen, a small and hard quadrupolar molecule, is accommodated in water with little change in the critical temperature. For oxygen and nitrogen weak temperature dependencies of the coexistence curves of binary mixtures show Ising-like behavior with the same exponent \( \beta \approx 0.326 \) as found for L–G coexistence curves of binary mixtures. This is but one example for the principle of isomorphism of the critical anomalies of pure fluids and mixtures.

In the present context, the major importance of these results is that large Ising-type critical anomalies are significant for supercritical aqueous solutions. While some equations of state for mixtures explicitly include asymptotic Ising behavior, crossover theories in analogy to that for pure water are lacking. Even if the nature of the crossover in mixtures would be elucidated in detail, the formulation of such a global equation of state as a function of temperature, pressure, and composition would be an appreciable challenge. We therefore have to rely on classical approaches, and hope that they are flexible enough to absorb the effects of critical anomalies in their regressed parameters.

### 3.4. Equations of State

Because accurate experimental data are not easily acquired, it is desirable to have a predictive equation of state for supercritical aqueous solutions. The need for predictive power requires at least semi-empirical approaches with parameters of some physical meaning. As for one-
component systems, a generalized formulation in terms of the Helmholtz energy $A(T,V,x)$ would provide the most appropriate form. In contrast, equations of state for mixtures usually begin with pressure-explicit relations of the form $P(V,T)$ for the pure fluids, which are then adapted to mixtures by introducing mixing rules.[1] The integration of these equations then allows chemical potentials, fugacities, or activities, to be calculated, which in turn, provide two- and three-phase lines by applying standard thermodynamic conditions for phase coexistence.[28]

Many equations of state have been derived for supercritical fluid mixtures in general,[1] but not all are suitable for describing aqueous solutions. Although at supercritical states the peculiar properties of liquid water no longer play an important role, the conditions for an appropriate equation are stringent, because the components have very different polarities. We consider a prototypical equation[76] which provides good descriptions of experimental phase diagrams and volumetric properties in the homogeneous regime, and has some predictive power.[68,76,77] This equation combines the popular Carnahan–Starling term for repulsive interactions[78] with an attractive term based on composition-dependent virial coefficients $B_i$ and $C_i$ of the square-well potential $\eta = (\pi/6)N\alpha x^3$ is the packing fraction, calculated from an core diameter $\alpha x$ averaged over the core diameters of the components. The diameters $\alpha x$ and depths $\epsilon x$ of the square-well potentials for the like-particle interactions $(i=j)$ are derived from critical data of the pure components. Parameters for unlike-particle interactions $(i \neq j)$ are determined by customary mixing rules: The energy parameter is estimated from the geometric mean, $\alpha_{ij} = \tilde{\epsilon} (\alpha_i \alpha_j)^{1/2}$, of the pure component parameters, the size parameter is estimated from the arithmetic mean, $\alpha_{ij} = (\alpha_i + \alpha_j)/2$. For accurate descriptions, the mixing rules are usually modified by adjustable parameters $\tilde{\epsilon}$ and $\zeta$, which makes them somewhat empirical. In practice, similar values of $\tilde{\epsilon}$ and $\zeta$ may apply for homologous solutes. The approximations limit this equation of state, and many similar equations, to high temperatures. No accurate equation for aqueous solutions spans the total range from normal to supercritical conditions.

$$P = \frac{RT V_x^m}{\left(V_x - V_{\text{ref}}\right)^3} + \frac{RT}{V^m_x - V^m_{\text{ref}}} \frac{B_i}{C_i}$$

Many other equations of state have been suggested. As an interesting example, we quote a recent equation for binary and multicomponent mixtures by Duan, Moller, and Weare,[79] which was shown to rationalize data up to 2 GPa and 2000 K, even for aqueous multicomponent mixtures.[80] A particularly interesting feature is that this equation is calibrated, among others, against data from MD simulations.

### 3.5. Homogeneous Supercritical Solutions

There is much interest in the bulk and molecular properties of homogenous mixtures of water with nonpolar solutes, both with regard to applications and to the understanding of molecular interactions between water and nonpolar solutes. As noted in Section 3.2, some experimental techniques for measuring phase-transition curves also enable the determination of volumetric properties in the homogenous regime. Thus, many studies of phase transitions also report on the $PV\tau_x$ relation.

Results of volumetric experiments are usually expressed in terms of excess molar volumes, $V^E$, which reflect deviations from additive volume behavior of the components upon mixing at constant pressure and temperature (the bar over the symbol denotes molar quantities). Excess molar volumes of supercritical mixtures with nonpolar compounds are positive, which indicates a volume expansion upon mixing. Usually excess molar volumes decrease at high pressures.

If $V^E$ is known, the excess molar Gibbs energy $G^E$ is obtained by integration over the pressure starting from a known reference state [Eq. (10)].

$$G^E(T,P,x) = G^E(T,P_{\text{ref}},x) + \int_{P_{\text{ref}}}^{P} V^E(T,P,x)\,dP$$

Partial derivatives of $G^E$ with respect to $P$, $T$, and $x$ then allow the calculation of chemical potentials, and fugacity and activity coefficients, which control chemical equilibria and phase behavior. Owing to large non-ideal behavior an account of activity or fugacity coefficients in computations of chemical equilibria or phase equilibria is indispensable, even at the qualitative level.

In principle, such calculations do, however, not differ from routine calculations performed at normal conditions, where a plethora of excess Gibbs energy models is available for modeling.[28] There are, however, some pitfalls in treating highly dilute solutions near the critical point of pure water, where some properties, such as the chemical potential of the solute, show diverging behavior. This can result in counterintuitive behavior. These subtleties are a relatively new insight, and the literature is full of misinterpretations in terms of dramatic structural changes in supercritical aqueous solutions, when approaching high dilution. The problems can be cured by proper reformulation of the theory.[72]

Limiting the discussion to more concentrated solutions, where such subtleties can be ignored, the excess Gibbs energies of aqueous solutions of nonpolar solutes are large and positive, as illustrated in Figure 12 for $H_2O + O_2$.[81] Because the excess volumes are positive, this non-ideal behavior increases with increasing pressure. In most cases the observed values are far higher than the typical excess Gibbs energies of binary liquid mixtures at room temperature. In conventional interpretations such strongly positive excess Gibbs energies are attributed to strong self-aggregation and clustering of the like particles.

Spectroscopic data that could provide information on molecular clustering are completely lacking. Some important information comes, however, from dielectric-constant data for aqueous solutions of benzene.[46] At 200 MPa and 673 K, the dielectric constant of pure water is $\varepsilon = 20$ which corresponds to that of many polar solvents at normal conditions. Figure 13 shows that, by adding benzene, $\varepsilon$ decreases rapidly at constant pressure. The strong asymmetric shape of the
composition dependence is retained at lower pressures, until at 20 MPa and 673 K the dielectric constant of pure water no longer differs greatly from that of benzene. Goldman and Joslin\[81\] used a theory based on a density expansion of the dielectric constant to describe these data in terms of molecular aggregation.

### 3.6 Multicomponent Mixtures

Many systems of interest in chemistry, geochemistry, and engineering contain more than two components. Because the number of data points needed for the characterization of multicomponent systems is largely increased, theoretical efforts are even more profitable. Many equations of state can be extended to multicomponent systems in a straightforward way, and in favorable cases, information on the binary subsystems is sufficient to describe the behavior of ternary and multicomponent systems. Illustrative examples are studies dealing with the systems $H_2O + N_2 + C_6H_{14}$,\[82\] $H_2O + N_2 + CH_4 + CO_2$,\[82\] or $H_2O + N_2 + CH_4 + CO_2$.[80] This success gives confidence for predictions made on systems where experimental data are scarce or absent. The system $H_2O + H_2 + O_2$ is an important example of interest in diverse fields, for example, for modeling of jet propulsion. Figure 14 shows the computed phase diagram of at 644 K.\[83\] The side planes of the prism represent heterogeneous areas of the binary subsystems $H_2O + H_2$ and $H_2O + O_2$, for which some experimental data are available. Once the parameters of the binary subsystems are fixed, properties such as phase-transition curves of the ternary system, corresponding to states inside the prism, can be computed.

A substantially different behavior is found if one of the components is a salt. The addition of salts to supercritical aqueous solutions leads to "salting-out" phenomena, which are, for example, of considerable interest for mineral formation in hydrothermal fluids. Figure 15 illustrates salting-out effects in $H_2O + CO_2 + NaCl$.[84] It shows experimental phase boundaries for 4 and 48 mol% of $CO_2$ in water, and their displacement by $NaCl$. At 48 mol% $CO_2$ the addition of only 6 wt% of $NaCl$ (relative to water) extends the heterogeneous regime by 100 K. Even larger shifts have been observed for methane.[85] As such experiments are extremely difficult and time-consuming, there seems to be no substitute for modeling. There are some promising results in this direction, for
example for \( \text{H}_2\text{O} + \text{CH}_4 + \text{NaCl} \) and \( \text{H}_2\text{O} + \text{CH}_4 + \text{CO}_2 + \text{NaCl} \). In principle, such modelings suffer, however, from the lack of information on interactions between salts and nonpolar substances. It is usually assumed that the solubility of salts in nonpolar fluids is completely negligible.

It is clear that many interesting applications of supercritical aqueous solutions concern geochemical problems. Some geologically important hydrothermal fluids contain up to ten or more species at concentrations sufficiently high enough to influence phase transitions and thermodynamic properties. A fascinating example for the power of modern experimental technologies and theoretical modelings is the study of hydrocarbon genesis in the Earth’s mantle. It is a common belief that the hydrocarbons of natural petroleum result from biotic organic materials under the pressure of deposited sediments. Recently, evidence has been reported that in the high-temperature, high-pressure hydrothermal solutions containing \( \text{CaCO}_3 \) and \( \text{FeO} \), methane can be formed in an abiogenic pathway.\(^{[87]}\) Scott et al.\(^{[88]}\) have now demonstrated the formation of methane by in situ Raman spectroscopy in a diamond anvil cell at pressures between 5 and 11 GPa and temperatures between 500 K and 1500 K, a range which includes the typical conditions found in the Earth’s mantle at a depth of about 30 km. The observations were further supported by thermodynamic calculations based on equations of state which were modified to allow for chemical reactions.\(^{[89]}\) The results suggest that an abiogenic pathway may indeed contribute to the Earth’s total methane budget. The potential exists for formation of heavier hydrocarbons in hydrothermal systems from methane as a precursor.

4. Aqueous Solutions of Electrolytes

4.1 Salt Solubility

Coulomb interactions between charged species are much stronger and of longer range than the interactions between uncharged species. Among others, these strong interactions lead to high critical temperatures for salts which cannot be reached by experiments. In contrast to the situation encountered with non-ionic fluids, water is then much more volatile than the solute. Even the temperatures of the normal melting points (S–L) and solid–liquid–gas (S–L–G) triple points of simple salts usually exceed the critical temperature of water. Thus, liquid–solid equilibria in supercritical water cannot be ignored and lead to complex phase diagrams, often involving more than one solid phase. Experiments are usually restricted to the water-rich regime.

For many applications it suffices to know the gross phase behavior. This behavior mainly depends on whether the vapor-pressure curve of the saturated solution, that is, the S–L–G three-phase line, cuts the L–G critical line (type 2) or does not cut it (type 1).\(^{[90]}\) In the type 2 case salts are practically insoluble in dense supercritical water, in the type 1 case they are soluble. Even the type 1 electrolytes will precipitate, however, if the water density is decreased. Thus, instead of L–L equilibria, as encountered with non-ionic solutes, solid–liquid equilibria are now decisive for the fate of the L–G critical curve. Table 1 classifies some important salts according to their solubility behavior.\(^{[90]}\) Soluble salts of type 1 includes most alkali and alkaline-earth halides and the hydroxides. The group of practically insoluble salts of type 2 includes, among others, the sulfates.

| Table 1: Classification of salts according to their solubility behavior in supercritical water.\(^{[90]}\) |
|-----------------|-----------------|
| Type 2 (insoluble) | Type 1 (soluble) |
| LiF, NaF | KF, RbF, CsF |
| LiCl, NaCl, KCl, RbCl, CsCl | LiBr, NaBr, KBr, RbBr, CsBr |
| CaF\(_2\) | CaCl\(_2\), CaBr\(_2\), CaI |
| BaCl\(_2\), BaBr\(_2\), BaI |
| Li\(_2\)CO\(_3\), Na\(_2\)CO\(_3\) | K\(_2\)CO\(_3\), Rb\(_2\)CO\(_3\) |
| Li\(_2\)PO\(_4\), Na\(_2\)PO\(_4\) | K\(_2\)PO\(_4\) |
| Li\(_2\)SO\(_4\), Na\(_2\)SO\(_4\), K\(_2\)SO\(_4\) | Rb\(_2\)SO\(_4\) |
| MgSO\(_4\), CaSO\(_4\) |

The most important example of a soluble salt is NaCl. Bischoff and Pitzer have summarized the available work on the NaCl + H\(_2\)O system and have discussed its phase behavior in detail. Today, the critical curve is known from fluid inclusion experiments to about 1100 K, corresponding to 30 wt % of NaCl.\(^{[91]}\) At all compositions, the three-phase line S–L–G runs sufficiently below the critical curve to avoid an interruption. Because liquid–liquid phase equilibria are absent as well, the critical curve of NaCl probably remains uninterrupted up to the critical point of NaCl above 3000 K. Rules of thumb developed for non-electrolytes predict an interruption whenever the ratio of the critical temperatures of the pure compounds exceeds a value of 2–2.5.\(^{[92]}\) For NaCl + H\(_2\)O this ratio is 5. Clearly, electrolyte solutions do not obey this rule.

As an example for an insoluble type 2 salt, Figure 16 shows the three-phase line S–L–G of MgSO\(_4\) as a function of the salt molarity \( m \) (mol per kg of water).\(^{[93]}\) The key for
understanding such phase equilibria is a negative temperature coefficient of the salt solubility at high temperatures. The solubility of MgSO₄ increases with increasing temperature up to about 343 K, but then decreases. This retrograde solubility implies that some salts of high solubility at ordinary conditions become sparingly soluble in hot water, so that in the segment of the phase diagram shown in Figure 16 the solid regime occurs at higher temperatures than the liquid regime. Salts such as Na₂SO₄ and Na₂CO₃ behave similarly. As a consequence the three-phase line will intersect the L–G critical line at a critical end point. Because at the critical end point the salt is present only in trace amount, this point is, in practice, indistinguishable from the critical point of pure water.

Many studies of such phase equilibria have been initiated by geochemists, but there is considerable overlap with systems of interest in chemical or industrial applications. Low salt solubilities form, for example, a major problem for the industrial realizations of the SCWO process, because the salts may plug the reactor or connecting lines. Transitions along homologous series should, however, be noted. For example, Table 1 shows that Na₂SO₄ and Na₂CO₃ behave similarly. As a consequence the three-phase line will intersect the L–G critical line at a critical end point. Because at the critical end point the salt is present only in trace amount, this point is, in practice, indistinguishable from the critical point of pure water.

4.2 Liquid–Liquid Phase Separations in Electrolyte Solutions

In principle, the possibility for critical-curve interruption by L–L equilibria in electrolyte solutions also exists. It is, however, a widespread belief that in electrolyte solutions such L–L phase equilibria are absent, because ion hydration stabilizes the solutions against such a decomposition. Actually, above 559 K the system UO₂SO₄ + H₂O separates into two liquid phases. For a long time, this demixing was attributed to disproportionation and hydrolysis of the uranyl ion. Today, it is known that it forms a generic feature of high-temperature aqueous solutions of multivalent ions, but is usually suppressed by the retrograde solubilities of the salts.

Support for this conjecture has come from experiments with MgSO₄, which is an important constituent of natural solutions. The analysis of thermodynamic data suggests the appearance of an L–L equilibrium above the retrograde three-phase line (S–L–G). Figure 17 shows this behavior in a diamond anvil cell. A pressure jump near the retrograde three-phase line S–L–G results in spontaneous liquid–liquid demixing, as indicated by droplet formation. Eventually, the formation of a solid phase gives a more stable state, so that on a longer time scale L–L demixing is followed by crystallization. The data indicate that the L–L coexistence curve is probably located 5–15 K above the retrograde three-phase line S–L–G. The estimated L–L coexistence curve is shown in Figure 16, that of UO₂SO₄ + H₂O is given for comparison.

From the applications perspective, such L–L phase equilibria can be handled in reactors more easily than solid–liquid equilibria. It should, however, not be overlooked that L–L phase separation may generate very concentrated, highly corrosive solutions. Historically, technical and corrosion problems caused by L–L phase separation of UO₂SO₄ +...
H₂O were an important drawback for considering this system as a basis for an aqueous homogenous nuclear reactor.

From the scientific perspective, the L–L coexistence curves are of great importance for understanding electrolyte behavior, and can serve as important targets for testing electrolyte theories. Theory shows that such equilibria are generic features of electrolyte solutions whenever the dielectric constant of the solvent is low. Thus, the phenomenon is not limited to high-temperature water, but is also present in non-aqueous solvents of low \( \epsilon \) under ordinary conditions. By well-known corresponding-states arguments, such systems have been used to mimic properties of supercritical aqueous solutions that are difficult to study directly.

### 4.3 Critical Anomalies in Ionic Fluids

Another remarkable difference between ionic and non-ionic fluids concerns the near-critical behavior. It has been noted in Section 3.3 that the behavior of binary solutions should be isomorphous to that of pure fluids, and thus should exhibit Ising-like behavior. According to the renormalization group analysis, Ising-like universality is a result of the short-range nature of molecular interactions. Thus, the Ising model applies to non-electrolyte interactions decaying with distance as \( 1/r^d \), but not to the \( 1/r \)-dependent Coulomb potential. The long-range nature of the Coulomb interactions could violate the critical point universality, and give rise to mean-field critical behavior. This problem provides an intriguing challenge for theory and experiment. It is also relevant for applications because the presence of mean-field behavior would remove many difficulties encountered in modeling non-ionic systems.

In assessing the problem, a look at the L–G critical behavior of metals may be fruitful. Early experiments for alkali metals suggested mean-field criticality, but more recently, highly accurate experiments by Hensel and coworkers for alkali metals and mercury have confirmed an Ising-like nature of the critical point. A rationale is that the electrons screen the Coulomb interactions between the ionic cores to such an extent that they restore Ising-like behavior.

In electrolyte solutions, the bare Coulomb interactions between a pair of ions are screened by the charges of the other ions. This effect is known as Debye-shielding. It enters, for example, into the Debye–Hückel-theory of dilute solutions, where it is accounted for by the concept of the “ion cloud.”

The problem of the effect of Debye-shielding upon critical behavior has given rise to much recent theoretical and experimental work; see a comprehensive review by Weingärtner and Schröer. From theory, a clear picture has not yet evolved because for sufficiently realistic models of an ionic fluid the necessary renormalization group analysis has not yet become feasible. Some experimental data for supercritical NaCl solutions seem to suggest mean-field behavior.

Based on corresponding-states arguments, it seems possible to exploit L–L equilibria in non-aqueous electrolyte solutions as model systems for supercritical water systems. By clever choice of the salt and solvent, L–L critical points can be generated near ordinary conditions. A much investigated system of this type is tetra-n-butylammonium picrate + \( n \)-dodecanol, which has an upper critical point of 336 K. Taking the coexistence curve as a target, it is necessary to discriminate between the exponent \( \beta = 1/2 \) in the mean-field case and \( \beta = 0.326 \) in the Ising case. To a good approximation, the coexistence curve in Figure 18 is cubic in the asymptotic range for comparison a parabolic curve is also shown.

From such measurements the issue of asymptotic critical behavior of ionic fluids may now be regarded as largely settled in favor of an asymptotic Ising-like critical character as found for non-ionic fluids. Applications usually involve states further away from critical points, where interesting differences between ionic and non-ionic solutes are indeed observed. Generally, crossover to mean-field behavior seems to be much faster for ionic than for non-ionic fluids.

### 4.4 Systems that are Continuously Miscible up to the Molten Salt

As in the case of non-ionic mixtures, there is great interest in characterizing the properties of salt + water systems over the complete miscibility range up to the molten salt. In practice, it is impossible to conduct such experiments at liquid-like densities with salts such as NaCl. At the normal melting temperature of NaCl of 1074 K, pressures higher than 1 GPa are necessary to compress water to a liquid-like density. Moreover, such states of high temperature and high density would be very corrosive. The equation of state of NaCl + H₂O only extends to 873 K, 400 MPa, and 25 wt% NaCl. For NaCl a few additional fluid-inclusion data have been reported for higher temperatures and pressures.
Low-melting organic salts allow the transition from dilute electrolyte solutions to molten salts to be studied at ordinary conditions, but their solution properties are not typical for ionic behavior. Moreover, the compressibility of such systems is too low to generate substantial density variations. A more suitable electrolyte is NaOH, which at normal pressure melts at 594 K. NaOH is completely miscible with high-density supercritical water, thus offering a broad homogeneous region for investigations. Volumetric data have been reported up to 673 K and 400 MPa. In contrast to solutions of nonpolar solutes, the excess volumes are negative, which indicates significant volume contraction upon mixing.

The excess molar Gibbs energies \( G^E \) of NaOH + H₂O in Figure 12 are negative, and exhibit a strongly asymmetrical shape for the concentration dependence with a minimum in the water-rich regime. The data yield ionic activity coefficients that differ greatly from unity at all compositions. In modeling chemical or phase equilibria, the consideration of activity corrections is therefore mandatory. The difference to the positive \( G^E \) values of nonpolar solutes is striking. The negative values seem to reflect a dominance of ion hydration over other interparticle interactions. More detailed interpretations are, however, difficult because molten NaOH of low compressibility is mixed with highly compressible supercritical water.

### 4.5 Electrical Properties

Since the first investigations of the electrical conductance of supercritical solutions of KCl, HCl, and KOH up to 1273 K and 1 GPa, this subject has been of continuing interest. Almost all conductance studies refer to dilute solutions, typically at molar concentrations of \( c \approx 0.01 \text{ molL} \) of the salt (referred to 298 K), which corresponds to a mole fraction of less than \( 2 \times 10^{-4} \). Figure 19 shows schematically the basic features of the molar conductance \( \Lambda \) of dilute solutions of alkali-metal salts, strong acids, and hydroxides plotted as a function of temperature and pressure. \( \Lambda \) is almost zero at low water densities, where neutral ions pairs are stable. Above 0.2 g cm⁻³, \( \Lambda \) begins to rise up to a maximum near 0.6 g cm⁻³, where the dielectric constant of water is high enough to push the dissociation equilibrium almost entirely to the side of the free ions. The decrease of \( \Lambda \) at still higher densities reflects the increase in the viscosity of the solutions. The maximum conductivity is an order of magnitude higher than that at ordinary conditions. The “Grotthus mechanism” of rapid H⁺ and OH⁻ ion transport via hydrogen bonds is less efficient at high temperatures.

For NaOH, conductance measurements have been performed up to the pure molten electrolyte. Figure 20 shows an isotherm of the molar conductance at 623 K at liquid-like total density as a function of the mole fraction of NaOH. At dense states, water still has an appreciable dielectric constant, and the initial segment of the conductance curve shows the typical high values of dissociated electrolyte solutions, which rapidly decrease with increasing salt concentration. Above 20 mol % of salt, the gradual replacement of water by NaOH has only a limited influence, and the conductance behavior is already similar to that of a molten salt. Conductance equations for electrolyte solutions fail in describing this conductance behavior over the complete miscibility range, as do some familiar expressions based on an analysis of the conductance–viscosity (“Walden”) product \( \Lambda \eta \).

If the water density is lowered, ion-pairing increases. The electrical conductance gives, however, no information on the configuration of the ion pairs. In favorable cases, Raman spectroscopy may provide such information, because intramolecular vibrations in molecular ions, such as NO₃⁻, are
influenced by contacts with other ions and by changes in hydration.[112] MD simulations may also contribute to the understanding of ion equilibria.[27] A broad range of ion configurations from contact ion pairs to solvent-separated ion pairs is usually found, but at low dielectric constant, contact ion pairs are preferably formed. Again, results for electrolyte solutions in non-aqueous solvents at normal conditions may indicate the phenomena to be expected in supercritical water.[97]

The high electrical conductance of supercritical aqueous solutions enables the electrolysis of water to \( \text{H}_2 \) and \( \text{O}_2 \). Such an electrolysis may, among others, be interesting for in situ generation of oxygen in oxidation processes. Experiments at supercritical conditions were performed in solutions of NaOH to 400 MPa and 803 K.[113] Figure 21 shows some results obtained with gold electrodes.

![Figure 21](image.png)

**Figure 21.** Electrical current density \( j \) as a function of potential \( U \) for aqueous solutions of NaOH of molar concentration 1 mol L\(^{-1}\) (referring to normal conditions) at 673 K (○), 573 K (□), 473 K (△), and 293 K (●). The results are obtained with gold electrodes at a surface ratio of the cathode to anode of about 1:100. The pressure is 400 MPa in all cases.

At 298 K, the current-density–potential curves show a transition from low current densities below the decomposition potential to strongly increasing current densities above the decomposition potential. The equilibrium decomposition potential is \( U^0 = 1.23 \text{ V} \) at 298 K and 0.1 MPa, but there are overpotentials. The equilibrium decomposition potential as well as the overpotentials decrease with increasing temperature. At high temperatures the potential curves become almost linear. The overpotential disappears, and current densities become very high. High temperatures reduce the influence of activation barriers, enhance transport processes, and reduce ion absorption at the electrodes. As a consequence, the electrodes are almost nonpolarizable above 673 K. The current densities of up to 35 A cm\(^{-2}\) obtained at cell voltages of about 2 V are two orders of magnitude higher than those obtained in industrial electrolyzers.

### 4.6 Transition-Metal Complexes

Knowledge of the ions present in solutions of transition-metal cations and of the stability regions of these aggregates is of particular interest in assessing the role of heavy-metal complexes in fields such as SCWO technology, metallurgy, or for understanding high-temperature corrosion. Spectroscopy in the visible (Vis) or ultraviolet (UV) range also provides a powerful means for investigating complex formation. For example, the hexaquo-complexes of Co\(^{2+}\) ions in aqueous CoCl\(_2\) solutions at normal conditions give pink solutions, while at 573 K and a modest pressure of 35 MPa, the blue color of tetrahedral complexes prevails.[114] Similar changes in coordination have been found for other transition-metal cations by various spectroscopic methods.[112,114] and also by X-ray absorption fine structure (XAFS) experiments.[115]

These changes of coordination number are intriguing because unsaturated metal centers may coordinate with organic ligands, thereby catalyzing the degradation of these molecules in supercritical water. It remains to be investigated whether high-temperature catalysts of practical use for such processes can be developed.

### 4.7 Equations of State

Under normal conditions the thermodynamics of aqueous electrolyte solutions has been developed to a mature state, and theories are well founded in statistical mechanics. Practically all these theories are built upon ideas developed by Debye and Hückel in their theory of dilute electrolyte solutions, which, among others, results in the famous limiting law for the mean ionic activity coefficient.[104] Treatments of concentrated solutions rely on extensions of Debye–Hückel theory. Above all, a semi-empirical approach developed in many studies from 1973 onwards by Pitzer and co-workers[116,117] is now widely used. Pitzer’s theory combines a Debye–Hückel approach with a virial expansion for representing specific interactions.

Neither Pitzer’s model nor other approaches are suited for extension to supercritical conditions. Some essential problems in applications are of a technical nature, and can be cured by reformulation of the theory.[118] A more fundamental problem is that all these approaches rely on a Debye–Hückel-type reference system of free ions immersed in the dielectric continuum of the solvent. A reference system based on interactions between free ions seems to be impractical in regions where most ions are paired. Anderko and Pitzer[119] have therefore gone a different way, by adopting a reference state based on dipolar hard spheres as models for ion pairs. This concept has been successfully applied to rationalize phase equilibria and \( PVT \) properties of binary and ternary supercritical systems.[119,120] A theory that spans the total range from normal to supercritical conditions requires the connection of this approach with the Debye–Hückel-type theories. Such a global approach is not yet available.

### 5. Conclusions

Dense supercritical water is a medium which provides an unusual variety of interesting phenomena. Continuous changes of thermophysical properties can be achieved by...
pressure variation, and result in transitions from “gas-like” to “liquid-like” behavior. With plausible extrapolations, the existing data base is sufficient to establish an equation of state to 1273 K and 1 GPa. From shock-wave experiments, there is even information on some properties of water at several thousand Kelvin and up to almost 200 GPa.

The ultimate aim is to explain macroscopic properties in terms of molecular interactions. In this regard, the advent of high-speed computers opens new ways. While simulations are not yet accurate enough for practical applications, they provide much insight into the molecular origin of the various phenomena. In this regard, the fluid structure of water and the underlying nature of the hydrogen bonds play a key role. It is now ensured by many experiments and simulations that hydrogen bonds exist in dense states far above the critical temperature of water.

The change in the thermophysical properties of supercritical water with temperature and density has dramatic consequences for its solvent behavior. At high-temperatures water looses the familiar high selectivity towards polar and ionic compounds, and in some range of temperature and pressure nonpolar compounds become highly miscible. Typically, at 673 K, all inorganic gases and simple organic compounds, if not destroyed, are completely miscible with water at pressures up to several 100 MPa. At high water densities some salts are highly soluble as well. This opens a window for generating homogeneous aqueous solutions with high concentrations of solutes of largely different polarity. This extraordinary behavior is, of course, impossible at ambient conditions, and forms the conceptual basis of innovative techniques such as SCWO technologies. Other interesting chemical applications can be conceived.

Because in many situations, one is fairly close to critical points, the challenge of incorporating the nonclassical critical nature of fluids into theories and data correlations still remains. There is now widespread recognition that such effects are not limited to the vicinity of the critical point, but in some cases extend to states far away. In this regard, many equations of state are deficient. While the asymptotic scaling laws now allow an appropriate description near critical points, the understanding of crossover to classical behavior further away is still a challenge. A detailed understanding of this interplay between universal critical phenomena on the one hand and molecular interactions on the other remains a problem.

In this context it should be noted that the Coulomb interactions in ionic systems are much stronger and of longer range than van der Waals interactions in non-ionic fluids. This situation gives rise to substantial changes in phase behavior associated with the high critical temperatures and pressures and the high melting points of the salts. While in most supercritical solutions of nonpolar solutes phase behavior only fluid phase equilibria occur, in supercritical electrolyte solutions solid–fluid equilibria often play a decisive role. This fact has major consequences for industrial applications because salt precipitation in reactors is much more difficult to handle than fluid coexistence. Claims that the long-range nature of the Coulomb interactions even violates critical-point universality were, however, not confirmed by recent experiments.

As the strength of the Coulomb interactions crucially depends on their shielding by the dielectric constant of the solvent, a wide variety of ion configurations ranging from complete dissociation to complete association into neutral pairs can occur in supercritical water, which gives rise to large difficulties in formulating equations of state for supercritical aqueous electrolytes. For many transition metal ions, specific complex formation has to be considered as well. Pressure variation can lead to interesting changes in coordination which, in the light of possible prospects for catalysis, have yet to be explored in detail. Finally, the decisive role of supercritical solutions for geochemical processes should be emphasized again.

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[12] See, for example, D. T. Rickard, F. E. Wickman, Chemistry and Geochemistry of Solutions at High Temperatures and High Pressures, Pergamon, Oxford, 1981.
References


