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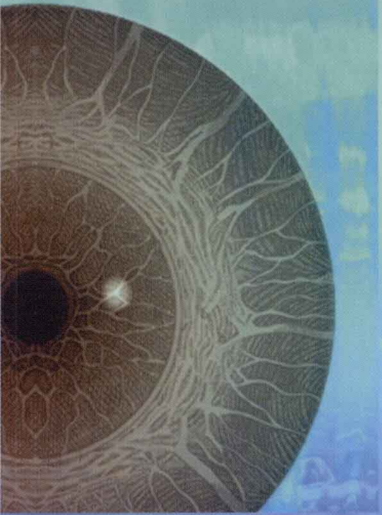

Inorganic Chemistry in Aqueous Solution

by JACK BARRETT

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Inorganic Chemistry in Aqueous Solution

JACK BARRETT

formerly of
Imperial College of Science, Technology and Medicine,
University of London

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Preface

Water is an important molecule. Seventy-one percent of the Earth's surface is covered by liquid water, it is the most abundant molecule, and it is a good solvent for polar and ionic substances. Samuel Taylor Coleridge's Ancient Mariner knew this:

Water, water every where,
Nor any drop to drink.

The lack of pure water for drinking purposes and the lack of water sufficiently pure for irrigating the land are major challenges for the human race.

This book offers no solutions to such severe problems. It consists of a review of the inorganic chemistry of the elements in all their oxidation states in an aqueous environment. Chapters 1 and 2 deal with the properties of liquid water and the hydration of ions. Acids and bases, hydrolysis and solubility are the main topics of Chapter 3. Chapters 4 and 5 deal with aspects of ionic form and stability in aqueous conditions. Chapters 6 (s- and p-block), 7 (d-block) and 8 (f-block) represent a survey of the aqueous chemistry of the elements of the Periodic Table. The chapters from 4 to 8 could form a separate course in the study of the periodicity of the chemistry of the elements in aqueous solution, chapters 4 and 5 giving the necessary thermodynamic background. A more extensive course, or possibly a second course, would include the very detailed treatment of enthalpies and entropies of hydration of ions, acids and bases, hydrolysis and solubility.

There are many tables of data in the text and the author has spent much time in attempting to ensure maximum consistency with the various available sources.

I thank Martyn Berry for reading the manuscript and for his many suggestions that led to improvements in the text.

Jack Barrett
Kingston-upon-Thames

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Some Thermodynamic Symbols and Definitions Used in the Text

Changes in the state functions (enthalpy, H, Gibbs energy, G, and entropy, S) are indicated in the text by a Greek delta, Δ, followed by a subscript that indicates the type of change. The various changes and their particular subscripts are defined in the table:

Change	*Symbol*
Formation of a compound or ion from its elements in their standard states	Δ_f
Formation of gaseous atoms of an element from the element in its standard state	Δ_a
Formation of the gaseous form of an element or compound from the standard state	Δ_v
Formation of a solid crystal lattice from its constituent gaseous ions	Δ_{latt}
Formation of a hydrated ion from its gaseous state	Δ_{hyd}
Formation of a solution of a compound from its standard state	Δ_{sol}

Other frequently used relationships are:

$$\Delta_{ion}H^{\circ}(M, g) = I(M, g) + 6.2$$

$$\Delta_{ea}H^{\circ}(X, g) = E(X, g) - 6.2$$

These convert internal energy changes to enthalpy changes.

The subscript ion refers to the ionization of a gaseous atom, M, and ea refers to the electron attachment to a gaseous atom, X, providing the values are quoted with units of kJ mol^{-1}. I(M, g) is the ionization energy of M, and E(X, g) is the energy change occurring when the atom X accepts an electron to become a negative ion: its electron attachment or electron gain energy. Other definitions and explanations of nomenclature are given as appropriate in the text.

Values of some constants:

N_A (Avogadro) = $6.022(14199) \times 10^{23}$ mol^{-1}

F (Faraday) = 96485.(34) C mol^{-1}

e (electronic charge) = $1.602(1773) \times 10^{-19}$ C

h (Planck) = $6.626(0755) \times 10^{-34}$ J s

R (molar gas) = 8.314(472) J mol^{-1} K^{-1}

The brackets indicate the fine accuracy of the values that are normally ignored in general calculations.

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1

Water and its Solvent Properties

This introductory chapter is about liquid water and some of its important properties – those that enable it to act as a good solvent for ionic and polar substances.

Aims

By the end of this chapter you should understand:

- What is meant by the terms solute and solvent
- That the water molecule has a significant dipole moment
- That the molecules in solid and liquid water interact by hydrogen bonding and that hydrogen bonding is responsible for the anomalous properties of water compared with the other hydrides of Group 16
- That the hydrogen bonding occurs because of the large dipole moment of the water molecule, and the presence of the unshielded protons
- That the self-ionization of water is slight and is consistent with the poor electrical conductance of the liquid
- That liquid water possesses a high relative permittivity which is associated with its property as a good solvent for polar molecules and ionic compounds
- That water is thermodynamically very stable and may act as solvent for a large range of compounds

1.1 Introduction

A **solution** consists of a **solute** dissolved in a **solvent**. The solute is recoverable from the solution, *e.g.* sodium chloride dissolved in water is recoverable by evaporating the solvent. In some cases the "solute" reacts with water and cannot be recovered by the removal of the solvent. In such cases the solution produced is of another solute, related to the initially dissolved substance. For example, sodium metal reacts with water to give a solution of sodium hydroxide. In general, polar molecules and ionic solids dissolve readily in polar solvents, and non-polar molecules dissolve readily in non-polar solvents. The ionic compound sodium chlorate (VII) ($NaClO_4$, sodium perchlorate) dissolves in water at 25 °C to give a **saturated solution** – one with the maximum solubility – containing 205 grams per 100 cm^3 of water.

Some reactions with liquid water are dangerous, that of sodium metal with water being one of them. As quoted in Martyn Berry's book *H_2O and All That*, one student wrote in an examination answer: "Sodium is so dangerous that it isn't handled by human beings at all, only by chemistry teachers".

Atomic mass units. All atomic masses are based upon that of the mass-12 isotope of carbon, ^{12}C. This is accepted to be equal to the **molar mass** of the isotope, $M(^{12}C)$ [$= 12 \times 10^{-3}$ kg mol^{-1}] divided by the Avogadro constant, N_A, *i.e.* $m(^{12}C) = M(^{12}C)/N_A$. The atomic unit of mass is 1 $m_u = m(^{12}C)/12$. The quantity $M(^{12}C)/12$ is known as the molar mass constant, M_u [$= 1 \times 10^{-3}$ kg mol^{-1}]. Relative atomic masses are symbolized as $A_r(X)$ and are equal to $m(X)/m_u$ or $M(X)/M_u$. Likewise, relative molecular masses are denoted by the symbol M_r(molecular formula) = molar mass/M_u.

Box 1.1 Solubility

The **solubility** of a solute may be expressed in different ways. It is the **concentration** of the solute in a **saturated solution** at a particular temperature (because solubility varies with temperature). A saturated solution at a given temperature is one that is in equilibrium with undissolved solute.

(i) **Molar concentration**, *c* (still sometimes called **molarity**, a term now forbidden by the International Union of Pure and Applied Chemistry). Applied normally to dilute solutions, this is the number of moles of the solute in 1 dm^3 (1 litre) of the solution, expressed in terms of moles per cubic decimetre: mol dm^{-3}. A typical dilute solution would be one with a concentration of 0.01 mol dm^{-3}.

(ii) **Molality**, *m*; this is appropriate for more concentrated solutions, and is the number of moles of the solute in 1 kg of the solvent. A solution containing 10 moles of solute in 1 kg of solvent would be 10 molal or 10 mol kg^{-1}.

(iii) **Mole fraction**, *x*; this is the concentration of a solute in terms of the number of moles of the solute expressed as a fraction of the numbers of moles of the solute and the solvent. A 10 molal aqueous solution would have a solute mole fraction of $10/65.509 = 0.153$, since 1 kg of water contains $1000/18.0152 = 55.509$ moles of water. [$A_r(O) = 15.9994$, $A_r(H) = 1.0079$]

Molality and mole fraction, as expressions of concentration of a solute, possess the advantage over molar concentration of being independent of temperature.

Worked Problem 1.1

Q A saturated solution of sodium chloride in water at 20 °C contains 36 g of the salt per 100 g of water. The density of solid sodium chloride is 2170 kg m^{-3} and that of the saturated solution is 1197 kg m^{-3}. The density of water at 20 °C is 998.2 kg m^{-3} [$A_r(\mathrm{Na}) = 22.99$, $A_r(\mathrm{Cl}) = 35.453$]

(a) Express the concentration of sodium chloride as (i) molar concentration, (ii) molality and (iii) mole fraction. (b) Calculate the change in volume that occurs when the solution is made from its constituents, and suggest an explanation for the change.

A (a) (i) The molar concentration of a saturated solution may be calculated from its density. The volume of the solution is calculated by dividing its mass by its density: $V = 0.136$ kg/1197 kg m^{-3} = 1.136×10^{-4} m^3 or 0.1136 dm^3. One dm^3 would contain 36/0.1136 = 316.9 g of NaCl. The molar concentration of the solution is 316.9/(22.99 + 35.453) = 5.422 mol dm^{-3}.
(ii) There would be 360 g NaCl dissolved in 1 kg of water. The molality of the solution is 360/(22.99 + 35.453) = 6.16 *molal.*
(iii) The mole fraction of sodium chloride in the solution is:

$$x_{\mathrm{NaCl}} = \frac{\dfrac{36}{58.443}}{\left(\dfrac{36}{58.443} + \dfrac{100}{18.015}\right)} = 0.0999$$

(b) One dm^3 of the solution has a mass of 1197 g, of which 316.9 g are NaCl, leaving 1197 – 316.9 = 880.1 g of water. The volumes of these constituents are $(316.9 \times 10^{-3}$ kg)/(2170 kg m^{-3}) = 1.4604×10^{-4} m^3 = 146.04 cm^3 NaCl and (0.8801 kg)/(998.2 kg m^{-3}) = 8.8169×10^{-4} m^3 = 881.69 cm^3 water, making a total volume of 146.04 + 881.69 = 1027.73 cm^3. There is therefore a contraction of 27.73 cm^3 when the solution is made. This indicates that there are interactions of the sodium cations and chloride anions with the solvent as they become **hydrated**.

α-D-Glucose, $C_6H_{12}O_6$, with its five **hydrophilic** (= water seeking) OH groups, shown in Figure 1.1, dissolves readily in water to the extent of 54.6% by mass at 30 °C, and sucrose at 100 °C is soluble in water to the extent of 83% by mass.

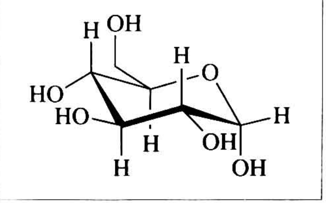

Figure 1.1 The α-D-glucose molecule

The alcohols, methanol, ethanol and 1- and 2-propanol are completely **miscible** with water, *i.e.* any composition is possible between 0% and 100% of the alcohol and 100% and 0% of water. As the **hydrophobic** (= water repelling) hydrocarbon content increases, alcohols become progressively less soluble in water, pentadecanol dissolving only to the extent of 1×10^{-5}% by mass and would be classed as insoluble. Non-polar tetrachloromethane dissolves in water at 25 °C to give an 8×10^{-3} mol dm^{-3} solution and hexane dissolves to give only a 1.3×10^{-4} mol dm^{-3} solution.

The hydration of ions – their interactions with water as solvent – is the subject of Chapter 2.

1.2 Liquid Water

Water is the most abundant molecular substance on Earth. The Earth's **hydrosphere** contains an estimated 1.41×10^{24} grams of water in all its phases, contained mainly by the oceans [97% as saline water covering

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70.8% of the Earth's surface] with only 2% existing in the solid state as polar ice and glaciers. Ground water, aquifers, lakes, soil moisture and rivers account for the very small remainder. Like all liquids and solids, water exerts a vapour pressure and at any time there are about 1.3 × 10^{19} grams in the atmosphere (0.0009% of the Earth's total) and it is replenished every 12 days or so.[1] This amount seems to be rather small, but if all the water vapour were to be precipitated evenly over the Earth's surface instantaneously as rain there would be a layer 2.5 cm thick. The vapour is responsible for a substantial fraction of global warming, the retention of energy in the atmosphere, in the absence of which the Earth's surface would be some 33 °C cooler on average.

The triatomic water molecule has a bond angle of 104.5° in its electronic ground state, and the O–H bond lengths are 96 pm. Its structure is shown in Figure 1.2(a). The electronegativity coefficients (Allred–Rochow)[2] of hydrogen (2.1) and oxygen (3.5) are sufficiently different to make the molecule **polar** with a **dipole moment** of 1.84 D [1 Debye (D) = 3.33564 × 10^{-30} C m]. The **dipole** of the molecule is shown in Figure 1.2(b), the oxygen end being negative with respect to the two hydrogen atoms. In addition to the normal van der Waals intermolecular forces that operate between molecules, the relatively "bare" protons of the water molecule and the electronegative – and so relatively electron-rich – oxygen atom allow the formation of hydrogen bonds between adjacent molecules in the liquid and solid states. Hydrogen bonds in water have bond enthalpies of about 20 kJ mol^{-1}, which is weak compared with the strengths of single covalent bonds, which lie in the region 44 (Cs–Cs) to 570 (H–F) kJ mol^{-1}. However, H-bonds are responsible for the abnormally high values of the melting and boiling points of water, considering its low relative molar mass of 18.

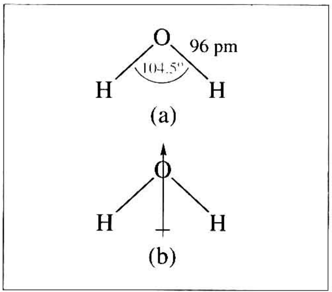


Figure 1.2 (a) The structure of the water molecule; (b) the water molecule dipole moment

Peter Debye was awarded the 1936 Nobel Prize for Chemistry for his work on dipole moments and on the diffraction of X-rays and electrons in gases.

Box 1.2 Dipole Moments

Polar molecules possess **electric dipole moments**, *e.g.* HF is a dipolar molecule with a partial charge of $+0.413e$ on the hydrogen atom and a partial charge of $-0.413e$ on the fluorine atom. The partial charges arise from the difference in electronegativity coefficients of the two atoms causing an unequal sharing of the valence electrons. The two partial charges are separated by a distance of 92 pm, the equilibrium internuclear distance otherwise known as the bond length. The dipole moment (normally the "electric" term is taken for granted) of the molecule, μ, is the product of the charge on the positive end, q, and the bond length, r:

$$\mu = qr \tag{1.1}$$

The dipole moment of the HF molecule is given by:

$$\mu(\mathrm{HF}) = 0.413 \times 1.602 \times 10^{-19}\,\mathrm{C} \times 92 \times 10^{-12}\,\mathrm{m} = 6.091 \times 10^{-30}\,\mathrm{C\,m}$$

The very small quantity is converted into a more easily quotable one by dividing the result by 3.33564×10^{-30}, giving 1.826 D for the dipole moment in Debye units. The Debye is a non-S.I. unit related to the S.I. unit C m by the relation:

$$1\,\mathrm{D} = 3.33564 \times 10^{-30}\,\mathrm{C\,m}$$

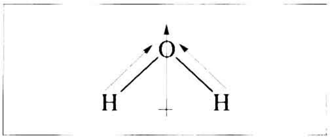


Figure 1.3 A diagram of the water molecule showing the dipole moment and its two constituent bond dipoles

The dipole moment of the water molecule is 1.8546 D or $1.8546 \times 3.33564 \times 10^{-30} = 6.19 \times 10^{-30}$ C m. Regarding this as the resultant of two O–H bond dipole moments, as shown in Figure 1.3, the charge separation in each bond is given by:

$$q = \frac{6.19 \times 10^{-30}}{2 \times 96 \times 10^{-12} \times \cos(104.5/2) \times 1.602 \times 10^{-19}} = 0.33e$$

This indicates that the charge separation is equivalent to a partial charge of $-0.66e$ on the oxygen atom and a partial charge of $+0.33e$ on both hydrogen atoms. This is to be expected from the difference in electronegativity coefficients of the two atoms in each bond.

Van der Waals forces operate between molecules, and are classified as: (i) dipole–dipole interactions or Keesom forces, (ii) dipole–induced-dipole interactions, and (iii) London dispersion forces which operate even between pairs of atoms as their electron distributions vary at any particular instant from perfect symmetry around their nuclei. They are responsible for the cohesion displayed between atoms of Group 18 (even helium can be liquefied) and between molecular compounds, and determine their melting and boiling points to a large extent. They operate in giant arrays such as metals and covalent lattices, *e.g.* diamond, but contribute only to a small extent to the total cohesion of the solid and liquid states in those cases.

Worked Problem 1.2

Q From the data given in Table 1.1, what evidence is there for hydrogen bonding in liquid and solid water?

Table 1.1 Melting and boiling temperatures (°C) for hydrides of the elements of Groups 14 and 16

Group 16 hydride	*M.p.*	*B.p.*	*Group 14 hydride*	*M.p.*	*B.p.*
H_2O	0	100	CH_4	−182	−161
H_2S	−85	−61	SiH_4	−185	−112
H_2Se	−60	−41	GeH_4	−165	−89
H_2Te	−49	−2	SnH_4	−150	−52

A A comparison of melting and boiling points for the series of hydrides of Groups 14 and 16 indicates the greater cohesion in the case of solid and liquid water. As the data for the Group 14 hydrides indicate, there is a general increase of the temperatures as the relative molecular masses increase, but superimposed on the similar trend in the Group 16 hydrides is the effect of hydrogen bonding in the case of water.

Over many years, rivers have carried the results of weathering of the rocks to the oceans, which have an enormous total ionic content as indicated by the data given in Table 1.2. Typically, when 1 dm^3 of seawater is evaporated to dryness, 42.8 grams of solid are produced, which contains sodium chloride (58.9%), magnesium chloride hexahydrate [$MgCl_2.6H_2O$] (26.1%), sodium sulfate decahydrate [$Na_2SO_4.10H_2O$] (9.8%), calcium sulfate (3.2%) and potassium sulfate (2%). Other compounds are present in minute amounts.

Table 1.2 The concentrations of the main constituent elements dissolved in sea water

Element	*Concentration*/mg dm^{-3}
Chlorine	19,400
Sodium	10,800
Magnesium	1290
Sulfur	905
Calcium	412
Potassium	399
Bromine	67
Carbon (as carbonate and hydrogen carbonate ions)	28
Strontium	8
Boron	4.4
Silicon	2.2
Fluorine	1.3

Worked Problem 1.3

Q Using the data given in the text, calculate the amount of sodium chloride that is potentially available from the oceans. Take the volume of the oceans to be 1.37×10^{18} m^3.

A The amount of available sodium chloride is $0.589 \times 1.37 \times 10^{18}$ (m^3) $\times 10^3$ (dm^3 m^{-3}) $\times$ 42.8 (g) $\times 10^{-3}$ (kg g^{-1}) $= 3.45 \times 10^{19}$ kg.

Currently, world annual production of the compound is about 2×10^{11} kg.

The major physical properties of water are given in Table 1.3. The abnormally high melting and boiling points already referred to are caused by hydrogen bonding in the solid and liquid phases, respectively. The structure of solid water (ice) formed at 0 °C and 100 kPa pressure, called ice-I_h, is shown in Figure 1.4.

h = hexagonal

Table 1.3 Major physical properties of water

Property	*Value*
Melting point (101 325 Pa pressure)	0 °C, 273.15 K
Boiling point (101 325 Pa pressure)	100 °C, 373.15 K
Temperature of maximum density	4 °C, 277.13 K
Maximum density	999.975 kg m^{-3}
Density at 25 °C	997.048 kg m^{-3}
Relative permittivity, ε_r, at 25 °C	78.54
Electrical conductivity at 25 °C	5.5×10^{-6} S^a m^{-1}
Ionic product $[H^+][OH^-]$ at 25 °C, K_w	1.008×10^{-14}
Enthalpy of ionization at 25 °C	55.83 kJ mol^{-1}
Standard enthalpy of formation, $\Delta_f H°$	−285.83 kJ mol^{-1}
Standard Gibbs energy of formation, $\Delta_f G°$	−237.1 kJ mol^{-1}

[a] 1 Siemen (S) = 1 Ω^{-1} (reciprocal ohm)

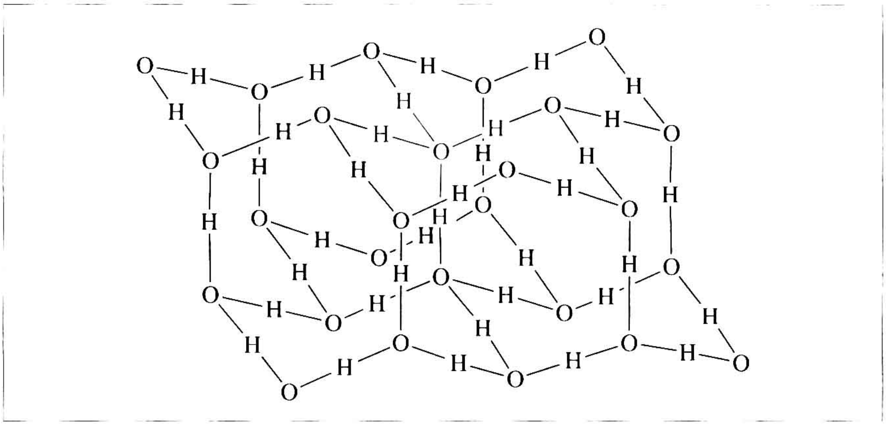
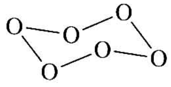


Figure 1.4 The structure of ice-I_h; the hydrogen atoms are placed symmetrically between the O–O pairs for simplicity

Ice-I_h consists of sheets of oxygen atoms arranged in a chair-like manner, as shown in the margin, with hydrogen atoms asymmetrically placed between all the adjacent oxygen atom pairs. The sheets are linked together with O–H–O bonds. Each oxygen atom is surrounded by a nearly tetrahedral arrangement of oxygen atoms; there are three oxygen atoms at a distance of 276.5 pm (within the sheets) and a fourth oxygen atom at a distance of 275.2 pm (linking the sheets.) The arrangement of the hydrogen atoms is disordered because of their asymmetrical placement between the pairs of oxygen atoms at any one time.

The somewhat open network structure of solid water determines that the density of ice at 0 °C is 916.7 kg m^{-3}. That of liquid water at 0 °C is 999.8 kg m^{-3} so solid ice floats on water, a fact noticed eventually by the captain of the *Titanic*! In liquid water at 0 °C there is still considerable



Natural water contains 0.15% of the mass-2 isotope of hydrogen: deuterium, ^2H or D. Heavy water (~100% D_2O) has its maximum density at 11.2 °C, an indication of the somewhat stronger deuterium bonding between adjacent molecules in the liquid phase. Solid D_2O melts at 3.82 °C and the liquid boils at 101.42 °C.

order because of the extensive hydrogen bonding. As the temperature rises, individual molecules have more translational, vibrational and rotational energy and need more space in which to move, thus causing most liquids (and solids) to expand and to have a lower density. This tendency is present in liquid water as the temperature increases, but additionally there is a progressive breakage of the hydrogen-bonded system that allows the open structure to collapse and to cause the density to increase.

Between 0 °C and the temperature of maximum density (4 °C) the hydrogen bond collapse dominates over the normal thermal expansion. At temperatures above that of the maximum density, thermal expansion dominates, and the density decreases progressively as the temperature rises.

The magnitude of the **relative permittivity** (or **dielectric constant**), ε_r of water is crucial to its solvent properties. In a vacuum, when two electric charges, q_1 and q_2 are brought together from an infinite distance to a separation r, the potential energy, E_p, is given by the **Coulomb's law** equation as:

$$E_p = \frac{q_1 q_2}{4\pi\varepsilon_0 r} \tag{1.2}$$

where ε_0 is the vacuum permittivity. It has a value of 8.854×10^{-12} $J^{-1}\,C^2\,m^{-1}$.

When the same procedure takes place in a medium such as liquid water, the vacuum permittivity in equation (1.2) is replaced by the permittivity of the medium. Normally the permittivities for a variety of solvents are expressed as relative permittivities, ε_r, at given temperatures. Some typical values of relative permittivites are given in Table 1.4.

Quantities such as ε_0 and the electronic charge, e, are accurately known to several decimal places, but are in general usage restricted to three decimal places: $\varepsilon_0 = 8.854 \times 10^{-12}$ $J^{-1}\,C^2\,m^{-1}$ and $e = 1.602 \times 10^{-19}$ C.

There are two liquids that have larger relative permittivities than water, namely anhydrous HF (84 at 0 °C) and formamide [or methanamide, $O{=}CH(NH_2)$] (109 at 20 °C), but they are very reactive to most solutes.

Table 1.4 Some typical values of relative permittivities

Compound	*Temperature/ °C*	*Relative permittivity, ε_r*
Water	25	78.54
Methanol	25	32.63
Liquid ammonia	− 33.4 (b.p.)	22.4
Propanone	25	20.7
CCl_4	20	2.24
Benzene	20	2.28
Hexane	20	1.89

The great significance of the high value of relative permittivity of water is explored in Chapter 2.

The electrical conductance of liquid water is very low compared with the values given by solutions of ionic compounds. Typically, the conductance of a 1 mol dm^{-3} solution of sodium chloride is about one million times higher than that of water. This illustrates the effect of the dissociation of ionic substances when they are dissolved in water:

$$Na^+Cl^-(s) \rightarrow Na^+(aq) + Cl^-(aq) \tag{1.3}$$

The ionic product of water, K_w, is related to the equilibrium:

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq) \tag{1.4}$$

in which liquid water dissociates slightly to give equal concentrations of hydrated protons and hydrated hydroxide ions. The equilibrium constant for the reaction is:

$$K = \frac{a_{H^+} a_{OH^-}}{a_{H_2O}} \tag{1.5}$$

in which the a terms represent the ratios of the activities of the species shown as subscripts to those at the standard activity of 1 mol dm^{-3}. The activity of liquid water in the solution is taken to be 1, because in dilute solutions $a_{\text{solvent}} = a^{\ominus}_{\text{solvent}}$ so the equation becomes:

$$K_w = a_{H^+} a_{OH^-} \tag{1.6}$$

and is known as the autoprotolysis constant or ionic product of water.

Activities of substances are used in strict thermodynamic equations because they properly and accurately represent the deviations from ideality exhibited by those substances when their concentrations (or partial pressures in the gas phase) are not infinitely small.

The **standard state** of a substance (symbol $^{\ominus}$) is its pure form (solid, liquid or gas) at a pressure of 1 bar (= 10^2 kPa; 1 Pa = 1 N m^{-2}) and at a specified temperature. If the temperature is not specified, it is assumed to be 298.15 K or 25 °C. The standard molar activity of a solute is 1 mol dm^{-3}.

In dilute solutions the activity of an ion can be defined by the equation:

$$a = \gamma c / a^{\ominus} \tag{1.7}$$

where c is the molar concentration (in mol dm^{-3}) of the solute, γ is the **activity coefficient** and $a^{\ominus}$ is the standard molar activity of 1 mol dm^{-3}.

In very dilute solutions, γ may be taken to be 1.0 and the autoprotolysis constant may be formulated as:

$$K_w = [H^+(aq)][OH^-(aq)] \tag{1.8}$$

the square brackets indicating the molar concentration of the substance by the usual convention. The autoprotolysis constant of water is essential for the discussion of pH and the acid/base behaviour of solutes (dealt with in detail in Section 3.3).

The standard enthalpy change for the ionization of water is +55.83 kJ mol^{-1}, which means that the reverse reaction, which occurs when acids are neutralized by bases, is exothermic, *i.e.* $\Delta_r H^{\ominus} = -55.83$ kJ mol^{-1}. The corresponding change in standard Gibbs energy is -79.9 kJ mol^{-1}. The reaction:

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l) \tag{1.9}$$

is thermodynamically spontaneous.

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