N. F. VOZNAYA

Chemistry of Water & Microbiology

Mir Publishers Moscow

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ХИМИЯ ВОДЫ И МИКРОБИОЛОГИЯ

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Chemistry of Water & Microbiology

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PREFACE

This book deals with the theory and practice of the treatment of natural waters and sewage. The problems discussed will help experts in the field of water-supply and sanitation to predict new trends of the processes involved, to assess their efficiency, and to choose the most suitable method.

The objects of this course are as follows:

(a) acquainting students with modern concepts of the physico-chemical processes occurring between various substances contained in natural waters and sewage;

(b) acquaintance with the principles of analysis of natural waters and sewage and with the utilization of the results obtained to assess the quality of water, to choose the right method of purification, and to predict the effect of water on building materials and structures;

(c) acquaintance with modern methods of treatment of natural waters and sewage and their disinfection;

(d) providing generalized concepts of bacteriological and biological analyses of waters and biological methods of the treatment of sewage.

This is the second edition of the book. It has been revised and enlarged significantly. The section "Microbiology" has in particular been enlarged.

The author takes this opportunity to express her gratitude to T. L. Simakova, Doctor of Biology, for her valuable assistance in the section "Microbiology", and also to Candidates of Science, L. B. Dolivo-Dobrovolsky, M. F. Rodicheva, and I. N. Churbanova for reading the manuscript and giving some useful advice.

Nadezhda F. Voznaya

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CONVERSION OF SOME UNITS USED IN THIS BOOK

Definition	Units	SI units	Conversion factor
CGS System			
Mass	g	kg	10^{-3}
Length	cm	m	10^{-2}
Force	dyne	n	10^{-5}
Surface tension	dyne/cm	N/m	10^{-3}
	erg/sq. cm	J/sq. m	10^{-2}
Viscosity	sentipoise	$N \times sec \times m^{-2}$	10^{-3}
Arbitrary Units			
Dipole moment	10^{-18} el. st. units$\times$cm	m$\times$sec$\times$A	0.333×10^{-29}
Osmotic pressure	atm	N/sq. m	1.0133×10^{5}
Pressure	mm Hg	N/sq. m	1.333×10^{2}
	atm	N/sq. m	1.0133×10^{5}
Specific conductance	$Ohm^{-1} \times cm^{-1}$	$Ohm^{-1} \times m^{-1}$	10^{2}
Heat	calorie	J	4.187
Heat capacity	$cal \times mole^{-1} \times deg^{-1}$	$J \times kmole^{-1} \times deg^{-1}$	4.187×10^{3}
Thermal conduction	cal/cm$\times$sec$\times$deg	$J \times m \times sec^{-1} \times deg^{-1}$	4.187×10^{2}
Radius	Å	m	10^{-10}
Entropy	$cal \times deg^{-1} \times mole^{-1}$	$J \times deg^{-1} \times kmole^{-1}$	4.187×10^{3}
Enthalpy	$kcal \times mole^{-1}$	$J \times kmole^{-1}$	4.187×10^{6}
Work performed by a system	$l\text{-}atm \times mole^{-1}$	$J \times kmole^{-1}$	1.0133×10^{5}
	$kcal \times mole^{-1}$	$J \times mole^{-1}$	4.187×10^{6}
Gibbs free energy	$kcal \times mole^{-1}$	$J \times kmole^{-1}$	4.187×10^{6}
Volume	l	cu. m	10^{-3}
Molality, molal concentration	$mole \times g^{-1} \times 10^{-3}$	$kmole \times kg^{-1} \times 10^{-3}$	1.0

Important Physical Constants

Universal gas constant, $R = 8.315 \times 10^{3}$ J/kmole$\times$deg
Boltzmann constant $K = 1.38 \times 10^{-23}$ J/deg
Avogadro number, $N_A = 6.024 \times 10^{26}$ $kmole^{-1}$
Faraday number, $F = 9.65 \times 10^{7}$ C/kg-equiv

INTRODUCTION

The reserves of water on the Earth are immense, but this is mostly salt water which is unfit for drinking or irrigation purposes. The amount of fresh water is huge as well but its distribution over the globe is uneven. There are zones where the yearly precipitation exceeds the amount of water evaporated from the surface of the Earth, and conversely, areas are known where the amount of moisture evaporated is greater than the yearly precipitation.

The water demand for drinking and other domestic needs in a modern town varies from 100 to 500 litres a day per capita. But water is also consumed in industry and agriculture (irrigation, cattle breeding), and if the total water demand is thus considered, it increases 10-12 times per capita.

As man uses water, he pollutes it inevitably, and when the water is returned to the open bodies it contaminates natural water.

Water supply and sewage treatment were in a deplorable state in pre-revolutionary Russia. And it was only after the Great October Socialist Revolution that municipal and industrial water-supply systems were launched on a wide scale. Special reagents have been devised to treat water and researchers are now looking for methods by which water could be treated without any reagents (by ultrasound coagulation, magnetic treatment, electric discharge, electrophoresis, etc.).

The quality of water is now the concern of experts in all countries of the world. The decision of WHO's 29th session (May 1976) emphasizes that water delivered to the consumer should meet the high requirements of modern hygiene and should at least be free from pathogenic organisms and toxic substances.

The quality of water depends on the location of the source and the state of environmental protection in a given area.

The official movement of the environmental protection in the USSR was started in 1924 when the National Society of Protection of Nature was founded. The movement later spread from the Russian Federation to all the Republics united in the USSR. This spread was favoured by the incessant concern of the Soviet Government and the Communist Party.

All possible measures are being taken in the USSR to preclude the ingress of toxic substances into water bodies. But Thor Heyerdahl justly notes that there are no 'national waters' in the ocean, they are constantly moving, and while nations can divide the bottom of the ocean, they can never divide waters running above it. Sea currents do not mind political or national frontiers. Water constantly moves in the world ocean to transport poisons from one region of the globe to another. For example, DDT was used in the fields of East Africa but in a few months it was revealed in the water of the Bay of Bengali, i.e. at a distance of 6,000 km. Hence the polution control should be the object of great and incessant concern of all nations.

All effluents should be treated thoroughly before disposal. It is expedient that they should be reused as much as possible for all purposes where water of lower quality can be used. Even purified effluents can pollute water and they should be discarded only on the condition that no other reasonable use of them seems to be feasible.

Special attention should be paid to the search for methods of treating industrial effluents with raw and waste materials used in a particular industry.

All processes involved in the treatment of water and effluents are connected with physico-chemical and micro-biological conversions, and water-supply and sewage engineers must study and use them rationally to control water pollution.

CHAPTER ONE

WATER AND AQUEOUS SOLUTIONS

1.1. Water

The Internal Structure of the Water Molecule. The water molecule consists of hydrogen and oxygen. According to modern concepts of the atomic structure, the electron clouds in water molecules form an irregular tetrahedron. The oxygen atom assumes the central position and the two hydrogens are in the opposite angles of one of the cube faces. The hydrogens are arranged at an angle of 104°31′. Two of the eight electrons of the oxygen atom are found around the nucleus, two are bound with the hydrogen atoms, and two unshared pairs of electrons form branches arranged in the opposite direction with respect to the electron clouds of the hydrogens (Fig. 1.1). These cloud branches are the regions of concentration of negative charges and account for the hydrogen bonding between water molecules and other substances. The water molecule can also be described in terms of groups of electron orbitals (Fig. 1.2).

The electronic configuration of the second layer of the free oxygen atom is as follows: $2s^2$, $2p_z^2$, $2p_y'$, $2p_x'$; the charge density of the $2s^2$ electron pair is distributed in the sphere to the side of the inner electron shell, while the density of the charge of $2p_z^2$, $2p_y$, $2p_x$ electrons is distributed symmetrically about the mutually perpendicular axes x, y, and z. As the two hydrogens become bonded by $2p_y$- and $2p_x$-orbitals, the 90° angle increases due to electrostatic repulsion, this disturbance increasing hybridization. The valency angle, corresponding to the minimum potential energy of the molecule, and passing through the maximum electron density, increases with the participation of s-electrons in the valency state. The hybridization of p- and s-states stimulates redistribution of the charge on two unshared electron pairs of the oxygen atom to favour unsymmetrical removal of the charge from the oxygen nucleus in the direction away from the protons.

As the charge is distributed, a significant dipole moment (1.84 debye) arises in the molecule. This important parameter, and also the angle and the length of the bond are shown in Fig. 1.3.

If water molecules had no negatively charged branches of the electron cloud and the dipole moments, they could not interact between one another.

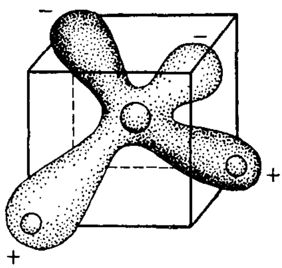


Fig. 1.1. The electron cloud of the water molecule

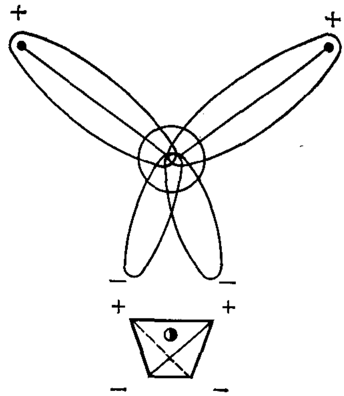


Fig. 1.2. The electron orbitals of the water molecule

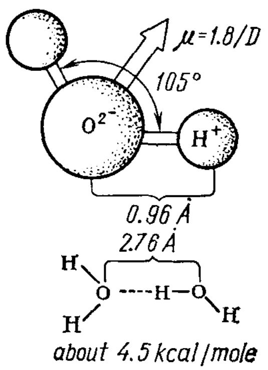


Fig. 1.3. The structure of the water molecule and the hydrogen bond

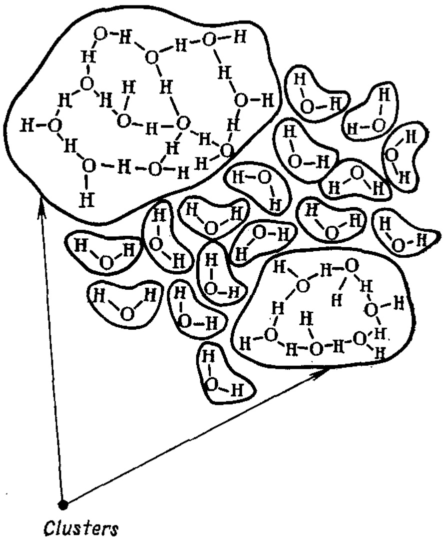


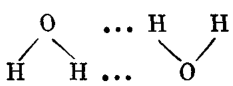
Fig. 1.4. The structure of liquid water in Frank-Wen flickering clusters

The Structure of Liquid Water. Various models have been proposed to explain the abnormal properties of water in the liquid state. Most of these show liquid water as a crystalline substance (liquid crystals). The ordered (crystalline) arrangement of particles in liquid water has been proved experimentally. As ice melts, its lattice is partly disrupted and the voids and the open structure of ice are filled with the liberated water molecules. The density of liquid water thus increases. It has been found that the amount of unbound molecules that fill the voids in the liquid water at 0°C is about 16 per cent of the total number of molecules.

Of special interest is the model which shows the structure of liquid water as flickering clusters* (Fig. 1.4), consisting of molecules interconnected by the hydrogen bonding and floating in more or less "free" water. Clusters are always present in fluid liquids, where they incessantly form and break up in accordance with the random thermal changes in the microparticles of the liquid. Frank and Wen have determined the half-life period of clusters, at 10^{-10}-10^{-11} second, which corresponds to the time of relaxation processes in water. This time is 100-1000 times greater than the period of molecular oscillations.

The classical theory of the structure of water by Bernal and Fowler claims that its maximum density is found at 4°C because at this temperature most molecules are bound in a quartz-like structure, while at other temperatures they have a tridymite-like crystalline structure producing a lower density.

Water molecules are characterized by *hydrogen bonding*. This is explained by the property of the hydrogen atom of interacting with a strongly electronegative element, for example, with the oxygen of another water molecule. As the hydrogen atom donates its only electron for a covalent bond with oxygen, it turns into a very small nucleus, almost devoid of the electron shell. For this reason it is not repelled by the electron shell of the oxygen of another water molecule, but on the contrary, is attracted to it and can interact with it. The greatest stability is found in twin molecules $(H_2O)_2$ formed with two hydrogen bonds:



(the dots indicate the hydrogen bond).

It should be noted that according to the existing concept of the hydrogen bond, it cannot be regarded as purely electrostatic.

According to the molecular orbital method, the hydrogen bond is formed by the dispersion forces, covalent bonding, and electrostatic interaction.

The Isotopic Composition of Water. Water is the product of the combination of two chemical elements, viz., hydrogen and oxygen. Both have isotopes.

Three isotopes are known for hydrogen: protium ^1H, having the mass of 1.007822 carbon units; deuterium $^2H(D)$, 2.0141; and tritium $^3H(T)$, 3.017001. The last is formed during nuclear decay.

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* Supramolecular complexes consisting of many molecules are called clusters.

The content of D in the natural mixture of hydrogen isotopes is 0.014-0.015 per cent.

Three isotopes are known for oxygen as well. Their mass numbers are 16, 17, and 18. Their proportions in the natural mixture of the isotopes are 2670:1:5.

Natural water is a mixture of molecules having the following formulas: $H_2{}^{16}O$, $H_2{}^{17}O$, $H_2{}^{18}O$, $HD^{16}O$, $HD^{17}O$, $HD^{18}O$, $D_2{}^{16}O$, $D_2{}^{17}O$ and $D_2{}^{18}O$.

Water with the chemical formula $D_2{}^{16}O$, $D_2{}^{17}O$ and $D_2{}^{18}O$ is known as heavy water, while water containing tritium is called super-heavy water, T_2O.

Heavy water is obtained by the prolonged electrolysis of natural water. It is more difficult to electrolyze than ordinary water and therefore concentrates in the cell because the deuterium ion loses its charge much slower than the protium ion.

The properties of heavy water are markedly different from those of common water. It freezes at 3.8°C, boils at 101.4°C, its density at 20°C is 1.1059 g/cc. Its maximum density is at +11°C. Salts are less soluble in heavy water. It produces an inhibiting action on vital processes in plants and animals. It is used as a moderator in nuclear fission processes.

Super-heavy water T_2O has the following (approximate) constants: m.p., +9°C; b.p., 104°C; density, 1.33 g/cc.

Hence water is a mixture of nine different molecules. Therefore none of the properties of water, especially its density, are constant, but instead depend on the proportion of each component in the mixture. For example, compare the densities of water obtained from various sources:

	(at 4°C)
Snow water	0.9999977
Rain water	0.9999990
River water	1.0
Ocean water	1.0000015
Water of a living body	1.0000012
Water of plants	1.0000017
Water of crystallization in minerals	1.0000024

Although the difference in the densities of pure water of various origins is comparatively small, it can be reliably measured on instruments.

The Physical Properties of Water. Pure water is a colourless (in thin layers) or bluish-green (in thick layers) clear liquid having neither odour nor taste.

The mass of 1 ml of purified river water is assumed to be the unit of mass and is known as a gram.

Some physico-chemical properties of water are given below:

Electrical conductivity at 18°C	4.3×10^{-8} ohm^{-1} $\times$ cm^{-1}
Freezing point at 760 mm Hg	0.00°C