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Solubility of oxygen in electrolyte solutions

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ABSTRACT. The latest advances in the study of the solubility of oxygen in water and in electrolyte solutions and of the influence of temperature and pressure on the solubility of oxygen are presented and surveyed. Advances in the development of experimental methods for the study of the solubility of oxygen are examined. The experimental results from studies of the influence of temperature and electrolyte concentration on the solubility of oxygen and their thermodynamic and molecular-statistical interpretation are described.

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I. Introduction

The reviews of Konnik[1] in this journal and of Wilhelm et al.[2] in a foreign journal were published in 1977. Konnik's review[1] was devoted to the application of salting out-salting using the theories most thoroughly developed at the time (the hydration, electrostatic, and "internal pressure" theories) in relation to oxygen at 298 K. The review of Wilhelm et al.[2] contains information about the solubilities of 57 gases, including oxygen, in pure water at a pressure of 101.325 kPa and at temperatures up to 350 K. A handbook, covering the experimental data on the solubility of oxygen in water and electrolyte solutions available in the literature up to 1978, was published in 1981.[3]

A critical review,[4] containing published data on the solubility of oxygen in water (at 273–573 K) and in electrolyte solutions at 298.15 K up to the end of 1980, appeared in 1983. A bibliographic index,[5] appeared in 1984, covering 108 literature sources (published up to the end of 1983) devoted to the study of the solubility of oxygen in water and in electrolyte solutions.

During the last decade, there has been a growth of interest in the solubility of oxygen, as shown by the number of publications (more than 200) during the last ten years (1979–1988) compared with the number of publications in 1969–1978 (about 80).

The Ist International Symposium on the Problems of the Solubility of Gases was held in 1984 in Canada. It was organised by the IUPAC Commission on Solubility.[6]

The existing reviews[1,2,4] did not deal with questions concerning methods for the study of the solubility of oxygen in liquids and also questions concerning the influence of the nature and concentration of electrolytes on the solubility of oxygen over a wide range of temperatures and pressures, as well as the problem of calculating the ionic coefficients of the salting out of oxygen from aqueous solutions.

The reviews as a rule considered the range of low temperatures and pressures. Since then, considerable advances have been achieved in solving the problem of the solubility of oxygen in water and in electrolyte solutions, namely in the development of experimental methods for the determination of the solubility of oxygen and in the study of the influence of the nature and concentration of electrolytes as well as temperature on the solubility of oxygen in electrolyte solutions. These thorough studies have led to the discovery of extrema, which are manifested particularly strikingly in electrolyte solutions. The extrema involve a change in the sign of the temperature dependence of the solubility of oxygen in water and in electrolyte solutions and the corresponding change from an exothermic to an endothermic heat of solution and also a change from salting out to salting in (or conversely) with increase in the concentration of certain electrolytes. Recently, the attention of investigators has been drawn to the explanation of these phenomena on the basis of molecular-statistical and thermodynamic theories of solutions.

The extrema are of interest for many branches of engineering and chemical and biochemical technology; their discovery should give rise to new approaches to the development of rational conditions for the passivation with oxygen of steel structures in aqueous media at high temperatures and to the deoxygenation of aqueous solutions (waste, industrial, and other solutions) in order to reduce their corrosive nature and also of conditions for the electrochemical synthesis of a number of substances and other processes.

The oxygen–water system is the recommended standard system in the study of the solubility of gases in water with which one can compare the solubilities of other gases. Such comparisons are essential in the adoption of new methods, the introduction of new gas analysers.[4,7,8] The degree of saturation of water with oxygen and the chemical and biochemical consumption of oxygen are important indices of the quality of different types of water.[9]

The existing reference literature,[10] reviews,[1,2] and textbooks,[11] which are widely used in various branches of science and chemical engineering, contain erroneous data on the solubility of oxygen. This was discovered in latest careful studies.[12] In particular, this can be seen in relation to the solubility of oxygen in NH_4Cl solution.[12,13]

The aim of the present review is to give an account of advances in the study of the solubility of oxygen in aqueous solutions of pure electrolytes and their mixtures, advances in the development of experimental methods for the study of the solubility of oxygen, and

in the analysis of experimental data on the solubility of oxygen in aqueous electrolyte systems and the influence of temperature, pressure, and the nature and concentration of electrolytes on the solubility of oxygen.

Particular attention has been devoted to the extrema observed in the study of the effect of temperature and electrolyte concentration on the solubility of oxygen and to the interpretation of the results on the basis of thermodynamic and molecular-statistical theories of solutions.

II. Methods of expressing the solubility of oxygen

More than ten methods of expressing the solubility of oxygen in liquids are known:[7,14,15] the Bunsen coefficient (α), the Ostwald coefficient (L), the Kuenen coefficient (S), the absorption coefficient (β), the Cook mass absorption coefficient (C_w), the mole fraction (X_2), the constants of Henry's law (K_H, K_2, and K_c) corresponding to the three forms of its mathematical formulation, the solvomolal concentration (c_{sm}), and the solvomolal absorption coefficient (A_{sm}). In addition, the volume and weight fractions and the molar and molal concentrations are sometimes used.

The Bunsen coefficient (α) is defined as the volume V_2 (adjusted to the normal conditions T = 273.15 K and p = 101.325 kPa) of the pure gas absorbed by a unit volume V_1 of the pure solvent and measured at a temperature T and a total pressure $p_{tot} = p_1 + p_2$:

$$\alpha = (V_2/V_1)(273.15/T), \ [cm_g^3/cm_s^3],$$

where p_1 and p_2 are the partial pressures of the solvent vapour and the gas at the temperature T. The subscripts g and s referred to the gas and the solvent.

The Ostwald coefficient (L) is defined as the ratio of the absorbed volume of gas V_2, measured at the pressure p_{tot} and the experimental temperature T, to the volume of the solvent under the same conditions:

$$L = V_2/V_1, \ [cm_g^3/cm_s^3].$$

There are four ways of expressing the Ostwald coefficient:[15]

$$L_V^\circ = (V_2/V_1^\circ)_{eq},$$

where V_2 is the volume of gas absorbed by a volume V_1° of the pure liquid at p_{tot} and T;

$$L_V = (V_2/V_1)_{eq},$$

where V_2 is the volume of gas absorbed by a volume V_1 of a saturated solution at p_{tot} and T: for dilute solutions and within an error of approximately 1%, the quantities L_v° and L_V differ insignificantly;

$$L_c = (c_2^L/c_2^V)_{eq}, \quad (1)$$

where c_2^L and c_2^V are the molar concentrations of the gas in the liquid and gas phases respectively (at p_{tot} and T). This way of expressing the Ostwald coefficient was used by Ben-Naim as the most suitable for discussion of hydrophobic interaction and the thermodynamic characteristics of the transfer of gases in solutions;[16]

$$L_c^\infty = \lim_{c_2^L \to 0} (c_2^L/c_2^V)_{eq},$$

this expression is a rigorous thermodynamic definition of the coefficient L_c [see Eqn. (1)]. The formula for the relations between the four different ways of expressing the Ostwald coefficient has been published.[15]

The Kuenen coefficient (S) is defined as the volume (cm^3) of gas at a partial pressure of 101.325 kPa (adjusted to 273.15 K and 101.325 kPa) dissolved in a solution containing 1 g of the solvent:

$$S = (V_2/m)(273.15/T), \ [cm_g^3/g_s],$$

where m is the weight of the solution.

The absorption coefficient (β) is defined as the volume of gas (measured at p_{tot} = 101.325 kPa and adjusted to 273.15 K and 101.325 kPa) dissolved in a unit volume of the solvent:

$$\beta = (V_2/V_1)(273.15/T)(p_2/101.325), \ [cm_g^3/cm_s^3].$$

The Cook mass absorption coefficient (C_w) is defined as the number of moles of gas (at p_2 = 101.325 kPa) dissolved in 1 g of the solvent:

$$C_w = (V_2/m_1 V_2^\circ)(273.15/T), \ [mol/g],$$

where m_1 is the weight of the solvent and V_2° the molar volume of the gas under normal conditions.

The mole fraciton (X_2) is defined as the ratio of the number of molecules of the dissolved gas (n_2) to the sum of the numbers of molecules of the dissolved gas and the solvent (n_1):

$$X_2 = \frac{n_2}{n_2 + n_1}. \quad (2)$$

The constants of Henry's law are described by the expression

$$K_H = \lim_{X_2 \to 0} (f_2/X_2) \cong \lim_{X_2 \to 0} (p_2/X_2), \ [Pa],$$

where f_2 is the fugacity of the gas. If the gas pressure does not differ very greatly from atmospheric, we have

$$K_H = \frac{p_2}{X_2(p_2)} = \frac{1}{X_2(p_2 = 1 \text{ atm})} \ [atm].$$

The two other ways of expressing Henry's law are as follows:

$$K_2 = p_2/c_2^s,$$

$$K_c = c_2^g/c_2^s = 1/L, \ [cm_s^3/cm_g^3],$$

where c_2^g and c_2^s are the concentrations of the gas in the gas phase at a pressure p_2 and in solution respectively.

The solvomolal concentration (c_{sm}) is defined as the ratio of the number of moles of the dissolved gas to 55.51 moles of the solvent:[14]

$$c_{sm} = \alpha \cdot 55.51 \, M_1/V_2^0\rho_1 = c_m M_1 \cdot 55.51/1000 = \\ = c_M M_1 \cdot 55.51/(1000\,\rho - c_M M_2) = X_2 \cdot 55.51/(1 - X_2),$$

where α is the gas concentration (ml under normal conditions per ml of the solvent), M_1 and M_2 are the molecular weights of the solvent and the gas (g mol^{-1}), ρ_1 and ρ are the densities of the solvent and the solution (g ml^{-1}), and c_M and c_m are the molar and molal concentrations of the gas in the liquid.

The solvomolal absorption coefficient (A_{sm}) is defined as the volume of the pure gas (V_2) (at a partial gas pressure p_2 = 101.325 kPa under normal conditions) absorbed in an amount of the pure or mixed solvent such that it contains 55.51 moles of the solvent:[14]

$$A_{sm} = \alpha \times 55.51 M_1/\rho_1 = L \times 273.15 \times 55.51 M_1/T, \quad (3)$$

where ρ_1 is the density of the pure or mixed solvent. The formulae

relating the different ways of expressing the solubility of oxygen are as follows:

$$L = \alpha T/273.15, \ [cm_g^3/cm_s^3],$$
$$X_2 = (RT/Lp_2V_1 + 1)^{-1},$$
$$K_H = RT/LV_1 + p_2, \ [Pa],$$
$$K_c = 1/L, \ [cm_s^3/cm_g^3],$$
$$\alpha = S\rho, \ [cm_g^3/cm_s^3],$$
$$C_w = \alpha/V_2^\circ\rho, \ [mol/g],$$
$$L = C_wV_2^T\rho,$$
$$X_2(p_2 = 101.325 \text{ kPa}) = C_wM_1/(1 + c_wM_1),$$

where R is the gas constant, p_2 the gas partial pressure, V_1° the molar volume of the solvent at a temperature T (cm^3 mol^{-1}), ρ the density of the solution (g cm^{-3}), V_2° the molar volume of the gas in cm^3 at 0 °C, V_2^T the molar volume of the gas in cm^3 at the temperature of the measurements, and M_1 the molecular weight of the solvent (g mol^{-1}).

The expressions for the solubilities of gases become more complex if the solvent contains a dissolved electrolyte.[17] For example, Eqns. (2) and (3) assume the form of Eqns. (4) and (5) respectively:

$$X_2 = n_2 \Big/ \sum_{i=1}^{k} n_i = n_2 \Big/ \left(n_2 + n_1 + \sum_{j=3}^{k} n_j \right), \quad (4)$$

where n_1 and n_2 are the numbers of moles of the solvent and the gas respectively and n_j is the number of moles of the dissolved electrolyte;

$$A_{sm} = \alpha\,(55.51\,M_1 + c_{sm,s}M_3)/\rho = L\,(55.51\,M_1 + c_{sm,s}M_3)\,273.15/\rho T, \quad (5)$$

where $c_{sm,s}$ and ρ are the solvomolal concentration and the density of a solution of an electrolyte with a molecular weight M_3.

X_2 and K_H have been most frequently used in recent years because these quantities are more convenient for calculating the thermodynamic characteristics of the dissolution of oxygen.

The Kuenen(S) and Cook coefficients, which have the advantage of being expressed in terms of weight concentrations, i.e. temperature has no influence on the concentration, suffer from the disadvantage that, on replacement of one solvent by another, the ratio of the dissolved oxygen and the solvent changes, which makes it difficult to compare the results. The absorption (β), Bunsen (α), and Ostwald (L) coefficients depend on temperature and they can therefore be used in thermodynamic calculations only to a limited extent. The solvomolal concentration (c_{sm}) combines the advantages of the molal concentration and mole fractions, both of which are widely used in the thermodynamics of solutions. The solvomolal absorption coefficient (A_{sm}) has been recommended to characterise the solubility of gases in pure and mixed solvents.[14]

In reviews, monographs, and original papers, one may encounter a wide variety of expressions for the solubility of oxygen in liquids, which is inconvenient when they are used and compared by different workers. Therefore it was suggested in 1975[18] that the mole fraction of the dissolved gas X_2 at a pressure of 101.325 kPa and a temperature T, at which the solubility measurements were made, be used as the standard unit of the solubility of the gas.

In the study of the thermodynamics of the dissolution of oxygen in water and in other pure solvents, X_2, K_H, or c_{sm} are used.

III. Methods for the study of the solubility of oxygen

In the study of the solubility of oxygen in liquids, methods are employed which are divided in the literature by convention into physical, chemical, and physicochemical.[18–23] They are being continually improved and developed.

The volumetric and manometric methods belong to the class of physical procedures. Their essential feature involves the measurement of the volume (pressure) of oxygen absorbed by the degassed liquid or desorbed from the liquid.[2,22–28] Chemical methods are based on the interaction of oxygen with reductants.[19,22,29]

Among physicochemical methods, spectroscopic, electrochemical, chromatographic, kinetic, radiometric, and mass-spectrometric methods as well as methods based on the paramagnetic properties of oxygen (EPR, NMR) are employed. In certain methods, the dissolved oxygen is evolved from the liquid, freed from the gases and vapours present, and its amount is measured.[30,31] During the last five years, the electrochemical methods (using voltammetric membrane sensors) have been most vigorously developed. Their advantages are speed, continuity, automation, and the possibility of carrying out measurements in reaction systems, natural and industrial waters, and biological liquids.

The error of the physical methods varies from several per cent to hundredths per cent.[4,32] The error of the determination of the solubility of oxygen usually varies in the range 1–2%, rarely in the range 0.1–0.2%; an error smaller than 0.1% has been achieved.[33] The disadvantages of the physical methods include the need to use large volumes of samples, the need to degas the liquid, to carry out repeated calibrations, to monitor the purity of oxygen, and to devise large thermostats, prolonged and laborious analysis, and the impossibility of carrying out continuous measurements of the concentration of oxygen.

1. Chemical methods

Among chemical methods, the iodometric method, first introduced by Winkler who described it in its classical form,[34] has come to be most widely used. Winkler's method is based on the reaction between dissolved O_2 and $Mn(OH)_2$ in a highly alkaline medium.

On acidification in the presence of iodide, the oxidised manganese hydroxide is reduced back to manganese(II) and the iodine liberated, whose amount is equivalent to the concentration of dissolved oxygen, is determined by titration with sodium thiosulphate. The error of the determination of the concentration of dissolved oxygen in pure water by Winkler's method is 0.03–0.05 mg $litre^{-1}$ (0.5%).[19,35] Disadvantages of the method are the impossibility of determining dissolved oxygen in inorganic (NH_3, Cl_2, etc.) and organic solvents and of assessing the influence of various substances (oxidants, reductants, carbonates, phosphates, borates, and fluorides).[29,35]

It is difficult to measure continuously the solubility of oxygen by this method. Winkler's method has therefore been frequently improved and its improvement is being continued up to the present time.[36–39] A novel apparatus has been devised for saturating water with oxygen and for establishing an equilibrium between the dissolved and gaseous oxygen with subsequent application of Winkler's method.[40,41] Modifications of Winkler's method have been developed in order to eliminate the interfering influence of oxidants and reductants[29] (substances which react with I_2 and I^- [42]) in the presence of carbonates, phosphates, borates, and fluorides[40,41] and Ca^{2+}, Fe^{3+}, NO_2^-, and CH_3COO^- ions,[43] as the concentration of oxygen in coloured solutions is varied,[44] and in the presence of

high concentrations of dissolved oxygen (more than 15 mg litre^{-1}) and organic substances.[45,46] The optimum conditions for the occurrence of the chemical reactions and the principal sources of errors and the methods used to eliminate them in the determination of the solubility of oxygen by Winkler's method have been described.[29,36,37,39,47,48] The use of potentiometric and amperometric titration as well as a photometric method to determine the end point has increased the sensitivity and accuracy of the method.[19,49]

Chemical methods not involving the oxidation of manganese(II) have been described.[19] However, their accuracy is lower than that of Winkler's method, which has come to be widely used in the practical investigation of the solubility of oxygen in pure water, in electrolyte solutions, and in natural, waste, and industrial waters. Winkler's method has been recommended[4,7,35,50] as the standard method by means of which one can test and calibrate other methods and instruments.

2. Spectroscopic methods

These methods are based on the selective absorption of light by substances whose colour changes on chemical interaction with oxygen. Indigocarmine, Methylene Blue, safranine T, β-sulphoanthraquinone, diphenyl-3,4-dihydroxy-L-β-phenylalanine, 3,3'-dimethylnaphthidine, and others have been used as substances of this kind.[23] The photometric determinations[38,51] of manganese(III) compounds (after the addition of complex-forming agents), of I_3^- ions formed when Winkler's method is employed, of iron(II) complexes of 4,7-dihydroxy-1,10-phenanthroline[52] and iron(II) complexes formed with an alkaline solution of catechol,[13] of cobalt(II) complexes of L-histidine and a tetraazamacrocyclic ligand,[53] and of a cobalt(II) complex of bis(salicylaldehyde)ethylenediamine deposited on a polymer or metallic (aluminium) film[54] have been described.[38,51] Compounds containing the $[Co(MoS_4)_2]^{3-}$ ion which change colour from green to black on interaction with O_2, can serve as indicators for oxygen.[55]

Optical sensors with an emulsified oxygen indicator in a polymer layer have been developed.[56,57] The spectroscopic methods are sensitive to impurities and require the maintenance of a specified pH for a specified exposure time, as well as calibration. The advantages of the spectroscopic methods are high sensitivity and the possibility of determining very low oxygen concentrations. The range of the measured oxygen concentrations is 0.005–0.4 mg litre^{-1} and the error is 2–15%. The concentrations of oxygen in water, in electrolyte solutions,[12,13] in natural and waste waters,[58] and in organic solvents[59] have been determined by these methods. However, the spectroscopic methods have been most widely used in the determination of low oxygen concentrations in the deaerated water in large thermal power stations and atomic power stations.

3. Optical fibre sensors

During the last 3–4 years, a new type of photometric device has been developed — chemical sensors (optical sensors) which consist of a section of a fibrous light guide, on the end-face or lateral surface of which a special reagent has been deposited. The interaction of oxygen with the reagent alters its optical characteristics and leads to the appearance of a signal in the absorption, reflection, or fluorescence spectrum.[60–69] Optical sensors can be used in combination with electrochemical sensors and are promising for the determination of oxygen in various media in industrial undertakings, especially in contaminated zones dangerous to health and in clinical and biomedical research.

4. The laser absorption method

This method is based on the absorption of radiation by the molecules of the substance analysed when the frequency emitted coincides with the frequency of the absorption line.[70] The amount of radiation absorbed is governed by the number of O_2 molecules. The concentration of oxygen mixed with other gases can be determined continuously by this procedure. The sensitivity of the method is 0.003 mg litre^{-1} and the error is 1–3%.

5. Luminescence methods

These methods for the determination of dissolved oxygen are based on the glow of the phosphors formed as a result of the chemical reaction of oxygen with certain substances. Such compounds are luminol (3-aminophthalic acid hydrazide), lucigenin (bis-*N*-*N'*-methylacridinium nitrate), 9,10-diphenylanthracene, acriflavin on rigidly porous sorbents, and derivatives of 4-bromo-1-naphthol extracted into cyclodextrin and fixed on cellulose and other carriers.[71–78] The emitted intensity depends on the pH of the solution and on the presence of impurities, temperature, and exposure time. In the luminescence analysis, it is therefore necessary to stabilise all these factors. The range of the concentrations of dissolved oxygen in water measured by the chemiluminescence method in the presence of lucigenin is 6.5–15 mg litre^{-1} and the error is 0.6%. The prolonged afterglow of acriflavin on silica gel [in the oxygen concentration range $(0.3-0.5)\times10^{-3}$ mg litre^{-1}] and on cellulose [in the range 0.01–0.2 mg litre^{-1}] has been used[72] to determine microconcentrations of oxygen.

A luminescence method for the determination of oxygen with the aid of an optical fibre fluorimeter has been reported.[73] The advantages of the luminescence methods over other physicochemical methods for the determination of the concentration of dissolved oxygen are high accuracy, the possibility of using small volumes of water samples to be analysed, and the automation of the measuring process.

6. Kinetic method

This method of determining the concentration of oxygen in aqueous solutions is based on the measurement of the induction period of the reaction catalysed by the copper complex of tetrabenzo[*b*,*f*,*g*,*n*][1,5,9,13]tetraazacyclohexadecyne, in which ascorbic acid is oxidised by oxygen.[79] The range of oxygen concentrations which can be determined is 0.5–32 mg litre^{-1} with an error of 0.1 mg litre^{-1}. Compared with Winkler's method, the kinetic method yields low solubilities of oxygen. Combined luminescence-kinetic methods, based on the quenching of the luminescence of dyes by oxygen, are being developed.[80]

7. Electrochemical methods

Electrochemical methods include amperometric, potentiometric, voltammetric, coulometric, and conductimetric methods.[19,20,81] The theory of these methods has been described in detail.[19,20] The electrochemical methods for the determination of oxygen in liquids have advantages over the chemical methods.[82] Firstly, the apparatus used in electrochemical methods gives rise to an electrical output signal, which can be applied in automatic regulation and control systems. Secondly, with the aid of electrochemical methods it is possible to determine continuously the rate of change of the concentration of oxygen. Thirdly, the composition of the liquid analysed hardly changes after contact with the electrochemical sensor.

Amperometric methods are based on the measurement of the diffusion current, which varies in the course of titration. The titration is carried out at a constant potential corresponding to the region of the limiting diffusion current of oxygen. Two versions of the amperometric methods are used. In the first version, one electrode serves as the indicator electrode and the other is used as the reference electrode; in the second version, two indicator electrodes are employed (biamperometric titration).[83] The advantages of the method are high sensitivity and accuracy, high speed of measurement, and the possibility of determining oxygen in coloured and turbid aqueous and non-aqueous solutions.

Potentiometric methods are based on the dependence of the e.m.f. of a galvanic cell on the concentration of ions in the electrolyte and on the oxidation-reduction processes occurring at the electrodes as a result of the reduction of the dissolved oxygen.[84–86] The thallium electrode has been thoroughly investigated for such purposes.[87–89] The concentration of oxygen in the range 0.4–20 mg litre^{-1} with a 5% error can be determined with its aid. However, owing to the toxicity of thallium, such electrodes have not come to be widely used.

A potentiometric sensor, whose electrolytic cell consists of a reference electrode (air/Pt, Na_2HPO_4 or $NaHCO_3$), a proton-conducting solid electrolyte [$Sb_2O_3.4H_2O$, $Zr(HPO_4)_2.H_2O$, and a Nafion membrane], and a platinum indicator electrode, has been proposed.[84] It has been suggested that the Cu(II)–Cu(I)–NH_3–H_2O oxidation-reduction system be used to determine oxygen in organic and aqueous organic solvents.[85] The disadvantages of the method are the need to devise a cumbersome apparatus to maintain a definite pH.

Voltammetric methods are based on the measurements of limiting diffusion current for oxygen reduction at the cathode at a constant potential. There are two varieties of the voltammetric method: with a mercury dropping electrode and with solid electrodes. The latter are used both without membranes and with gas-permeable membranes separating the electrochemical cell from the medium in which the concentration of dissolved oxygen is measured.

The sensitivity of the classical polarographic method with respect to oxygen is 0.05–0.1 mg litre^{-1} and the error is 0.02 mg litre^{-1}. The principal disadvantages arising in the use of the mercury dropping electrode are the difficulties associated with the measurements *in situ* and the risk of contaminating the test system with mercury. Solid electrodes are free from these disadvantages. the oxygen reduction limiting current at the cathode (Pt, Au, etc.) is proportional to the concentration of dissolved oxygen.[19] Carbon glass, boron carbide, or carbon paste "wall-jet" electrodes have been described.[90] A disadvantage of the membrane-free electrodes is the possibility of their contamination. Furthermore, the medium in which oxygen is determined must exhibit a sufficient electrical conductivity, since otherwise the true current may be appreciably altered under the influence of interfering substances. These disadvantages are eliminated when membrane voltammetric sensors (MVS), first proposed by Clark,[91] are used. Platinum, palladium, rhodium, and gold cathodes are used. Instead of expensive materials, it has been suggested that the cathode by made from nickel or nichrome (however, these require additional activation)[92] as well as carbon sitals, carbon fibres, and graphite.[82,93,94] Porous silver indicator electrodes have been proposed.[95]

The use of membranes suffers from a number of disadvantages: membranes are subject to mechanical damage; if membranes are made thicker in order to increase their mechanical strength, the inertia of the sensor increases; owing to the non-uniform thickness of the membrane, a scatter of the results of measurements is observed, which requires careful calibration of the sensor; the temperature, stirring, and pH of the solution influence the readings of the sensor.[96,97] Polyethylene and fluorinated polymers 10–25 μm thick have been used as membranes.[19,98] Membranes made of a multilayer polytetrafluoroethylene film containing 60% of Mn_4N,[99] cellophane,[100] silicones,[101] and other materials[102] have been put forward.

In biologically active media, membranes are coated by a biological film, as a result of which the sensitivity of the MVS diminishes. Hydraulic or mechanical purification is normally employed. Novel sensors, in which the membrane is freed from biocontaminants by means of gases, have been developed.[103,104]

Novel stirring devices have been proposed.[105,106] In order to increase the sensitivity of the MVS, the electrodes are activated.[107–109] A sensor without a layer of electrolyte between the cathode and membrane has been developed to diminish the influence of the pressure and vibration on the membrane.[96,110] A "protecting" electrode having the same size as the cathode has been introduced to diminish the influence of the background current between the cathode and anode.[111] The range of concentrations of the sorbed oxygen measured with the aid of the MVS is 0–50 mg litre^{-1}, the relative error is 1–6%, and the sensitivity is 0.05 mg litre^{-1}.[19] MVS with pulsed action have been developed.[112–114]

Electrochemical oxygen sensors have been standardised[115,116] and have been developed to the greatest extent. They are distinguished by simplicity in operation and can be easily transported. The application of MVS makes it possible to monitor rapidly and continuously the concentration of oxygen *in situ* under industrial, laboratory, and field conditions.[117] By virtue of high speed of the response of the MVS, they are used in systems for the automatic monitoring and regulation of the oxygen conditions in the purification of sewage, in aeration devices, and for the investigation of processes involving the biochemical consumption of oxygen (BCO) and of the intensity of the respiration of microorganisms in fish-farming water reservoirs.[82,97,118,119]

In addition MVS are widely used in biology and medicine.[101,120–122] Microbial amperometric sensors for the determination of biological consumption of oxygen have been developed.[123] The interest in MVS has grown continuously.[124–138] KP-101,[139] KL-115 N20-IOA,[140] KAP-105,[141] AKVA-S,[142] KM-105, KM-101, KM-201, and KMV-110[143] oxygen measuring devices are being manufactured in the USSR. AKP-205 apparatus has been developed for the determination of low oxygen concentrations in the range 0–0.5 mg litre^{-1} subject to an error of 0.001 mg litre^{-1}.[144]

Coulometric methods are based on the direct proportionality between the weight of the electrochemically reduced oxygen and the amount of electricity which has passed through the solution. Dissolved oxygen can be determined both directly in a water sample[145] and after its evolution from the solution.[146] In these methods, there is no need to have standard samples with dissolved oxygen. During the last three years, oxygen measuring devices using an indirect coulometric method have been created.[147] An advantage of the coulometric sensors over the MVS is the smaller influence of temperature on the oxygen reduction current. The temperature-induced changes influence the reproducibility of the MVS readings owing to the temperature-induced hysteresis in the membrane. The disadvantages of these methods are the impossibility

of measuring the concentration of dissolved oxygen *in situ* and the contamination of electrodes (unless special measures are taken before analysis to purify the water). The range of variation of the oxygen concentrations which can be measured is 0.03–66 mg litre^{-1}, the relative error is ~1%, and the duration of analysis is 4–5 min.

Conductimetric methods are based on the measurement of the electrical conductivity of either an electrolyte solution in which oxygen is dissolved or of metal oxides on interaction with the gaseous oxygen evolved from the solution.[81,148–151] These methods are highly sensitive and are suitable for the continuous determination of oxygen. However, they cannot be employed to determine the concentration of oxygen *in situ* partly owing to the contamination of the electrodes. When high-frequency conductimetry is used, this problem can be solved.[19] The disadvantages of these methods are the need for preliminary passage of the sample through an ion exchanger as a result of which dissolved oxygen may be lost; when thallium oxygen-measuring devices are employed, the high toxicity of Tl^+ is a disadvantage. The range of the measureable oxygen concentrations is 0.002–1 mg litre^{-1}, the sensitivity is to within 10^{-3} mg litre^{-1}, the error is several per cent,[19] and the analysis time is several minutes. Conductimetric methods are suitable for the determination of dissolved oxygen in very pure waters with a low electrical conductivity. Analysis of the literature[81,82,87,120] of the most recent years shows that conductimetric methods are relatively unpromising.

A second type of the conductimetric determination of oxygen is based on the dependence of the electrical conductivity of metal oxides (CoO, ZnO, TiO_2, etc.) and solid electrolytes ($Nd_\alpha Y_\beta F_\gamma O_\delta$, where $\alpha = 4.5–7.5$, $\beta = 4.5–7.5$, $\gamma = 14–24$, and $\delta = 6–11$) on the concentration of oxygen and temperature.[150–152] Oxygen can be determined continuously with the aid of these procedures.

New electrochemical methods. During the last five years, new electrochemical methods have been proposed for the measurement of the concentration of dissolved oxygen: the adsorption-kinetic methods[153,154] based on the measurement of the rate of displacement of the electrode potential under the influence of dissolved oxygen, the anodic inversion, pulse, and cyclic voltammetric methods,[155–160] the chronocoulometric method,[161,162] the chronopotentiometric method,[163] the chronoamperometric method using platinum microelectrodes,[164–166] inversion potentiometric analysis,[167,168] and the method involving the measurement of the electrical resistance or the pressure exerted by the semiconducting oxide film formed on the electrode in contact with the medium being analysed.[169,170]

8. Chromatographic methods

These methods are based on the use of the difference between the adsorbabilities of oxygen, other gases, and solvent vapour.[171–175] They are used for the determination of the weight concentration of the dissolved oxygen (in a mixture of gases) in liquids.[176,177] The analysis requires 10 μl of the liquid.[172] Chromatographic methods require special equipment and calibration and with their aid it is difficult to perform continuous measurements *in situ*. The error of the method is usually 3–15%,[175] sometimes 0.33–0.5%,[172,178] the sensitivity is 0.005–0.01 mg litre^{-1},[179] and the duration of the analysis is 10–15 min, sometimes 3–5 min.[174]

A new method has been proposed[180,181] for the determination of the concentration of dissolved oxygen—liquid–gas partition chromatography based on the filtration of the sample of the analysed solution through a column with a hydrophobic filler (for example, porous polytetrafluoroethylene) and the flushing of the column with the carrier gas. In contrast to the other types of the chromatographic process, in which the stationary phase is a solid or a liquid, in this case the gas deposited on the surface of a solid carrier serves as the stationary phase. This method made it possible to automate readily the extraction of dissolved oxygen from the liquid and to reduce appreciably the lower limit of the concentrations which can be determined—to $(2–4) \times 10^{-3}$ mg litre^{-1}. In certain cases, the chromatographic procedure is combined with other analytical methods.[182,183]

9. Resonance methods

The paramagnetic properties of oxygen made it possible to develop a series of methods and to construct on their basis automatic analysers for the measurement of the concentration of oxygen dissolved in water.[21,184] The range of measured concentrations is 0–50 mg litre^{-1} and the error is 3%. An advantage of this method is the rapid response (in ~1 s) to a change in the oxygen concentration.

The EPR method is based on the use of the phenomenon of the resonance absorption of the energy of electromagnetic waves by paramagnetic species in a steady magnetic field and is used for the continuous determination of oxygen dissolved in water at concentrations in excess of 0.3 mg litre^{-1}. The error is several tens per cent. The concentration of oxygen in liquid mixtures can also be determined by this method.[185] The EPR method is promising, since, in contrast to other gases, oxygen is paramagnetic and can be determined in a mixture of gases.

The NMR method is based on the measurement of the proton spin–lattice relaxation time τ of the paramagnetic species in solution. The time τ is linearly related to the concentration of dissolved oxygen.[186] However, the application of the EPR and NMR methods requires a complex apparatus. The rate of consumption and diffusion of oxygen in cells has been investigated with the aid of NMR.[187]

10. Radiometric methods

These methods are based on the determination of the radioactivity of the elements or compounds formed when nucleons or radioactive elements react with dissolved oxygen. When a liquid sample is irradiated with fast neutrons, ^{16}O is converted into the unstable isotope ^{16}N with a half-life of 7.35 s.

The advantages of the method include a high sensitivity ($2 \times 10^{-4}–2 \times 10^{-2}$ ml litre^{-1}) and the disadvantages include the need for special equipment and calibration. In another radiometric method, the radioactive ^{204}Tl isotope is oxidised by dissolved oxygen.[188] The decrease in the intensity of the emission from ^{204}Tl is directly proportional to the concentration of dissolved oxygen. Salts dissolved in water, which influence the solubility of Tl^+ compounds, have an interfering effect. Furthermore, the extent of the oxidation of thallium depends on the pH and the presence of oxidants.

The indirect determination of the oxygen dissolved in water by atomic absorption spectrometry is based on the interaction of oxygen with thallium and the determination of Tl^+ ions by atomic absorption spectrometry. The sensitivity of the method is 0.019 mg litre^{-1} and the error is 0.04 mg litre^{-1}.[189]

11. The mass-spectrometric method

This method is used when it is necessary to know the isotopic composition of oxygen.[190–195] It is highly sensitive and does not require calibration. The relative error is 2%. A disadvantage of the method is the need for complex equipment.

An isotope-spectroscopic method for the measurement of oxygen concentration has been reported.[196] The method consists in the metered introduction of a rare stable oxygen isotope into the gas analysed, the attainment of a uniform distribution of isotopes in the resulting mixture, and the determination of the isotope composition of oxygen on the basis of emission spectra. The principle of the method is the direct proportionality of the intensity of the spectral lines or bands emitted by the atoms or molecules to their concentration in the discharge, the latter serving as the source of light. The advantages and disadvantages are the same as in the mass-spectrometric method.

The analytical possibilities for the quantitative determination of oxygen dissolved in liquids using a laser microprobe have been investigated.[197] The range of concentrations which can be measured is 0.4–2 g litre^{-1} and the error is 5%.

IV. Results of the experimental study of the solubility of oxygen in water and in electrolyte solutions

The solubility of oxygen in water and in certain electrolytes has been investigated in numerous studies whose results have been compiled and discussed.[1–4,7,198] The solubility of oxygen in pure water and sea water and also in aqueous solutions of acids, alkalis, and salts of alkali and alkaline earth metals has now been studied most fully.[1,4,198]

1. Solubility of oxygen in water at different temperatures

In most studies, the solubility of oxygen in water was investigated in the temperature range 273–348 K at atmospheric pressure. With increase in temperature, the vapour pressure of water increases and it is more difficult to maintain a constant degree of saturation. This entails a decrease in the accuracy of the determination of the experimental solubilities of oxygen. Therefore it has been suggested that the oxygen solubility data[4] be expressed with different errors in two temperature ranges: with an average error of 0.30% at temperatures below 348 K and with an average error of 2% above 348 K. The International Standard ISO 5814-84 lists the solubilities of oxygen in water as a function of temperature (0–40%) and salinity (0–35 g dm^{-3}).[35]

In most studies, the gas used to saturate the solution with oxygen was air and the experimental solubilities of oxygen were adjusted to p_{O_2} = 101.325 kPa taking into account the vapour pressure of water. The use of air instead of pure oxygen is a disadvantage, since, together with oxygen, nitrogen and other gases (nitrogen, carbon and sulphur oxides as well as ammonia) dissolve and interact with water, which may alter the chemical compositions of the solutions and their pH. This factor has not been taken into account in all studies and special measures to purify the air saturating the solutions have not always not been taken. Therefore the studies in which pure oxygen was used to saturate the solutions are the most reliable and accurate. Furthermore, the air or oxygen supplied to the solution must be saturated with water vapour and at elevated temperatures must be heated. Such improvements of the methods have been described.[40,41]

Battino et al.[4] treated by least squares the most reliable experimental data from 15 literature sources in the range 273–348 K and obtained the following expression:

$$\ln X_2 = -64.21517 + 8391.236/T + 23.24323 \ln(T/100). \quad (6)$$

(average error 0.30%), where X_2 is the solubility (mole fractions) of oxygen in pure water and T is the temperature (in K).

Benson et al.[193] proposed the following equation for the description of the temperature dependence of the solubility of oxygen in water in the range 273–373 K:

$$-\ln X_2 = 3.71814 + 5.59617 \cdot 10^3/T - 1.049668 \cdot 10^6/T^2, \quad (7)$$

with an average error of 0.017%.

The solubilities of oxygen in water at 273–373 K, calculated[4] from Eqns. (6) and (7) are presented in Table 1.

The differences between the solubilities of oxygen in water which we calculated by Eqns. (6) and (7) are presented in Fig. 1 as a function of temperature. At temperatures below 323 K, the relative difference of the solubilities is 0.2–0.4%, which agrees with the error (0.3%) of the calculation of the solubility of oxygen by Eqn. (6). At temperatures above 328 K, greater discrepancies between the solubilities of oxygen calculated by the two formulae are observed. This shows that the representation of the oxygen solubility data in the two temperature ranges (273–348 and 348–573 K) proposed by Battino et al.[4] is not altogether correct. It is desirable to restrict the first range to 273–328 K. In this range, the average error of the solubility of oxygen in water does not exceed 0.30%.

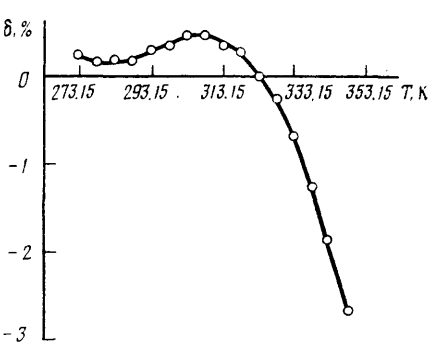


Figure 1. Temperature dependence of the relative difference δ between the solubilities of oxygen in pure water calculated by Eqns. (6) and (7).

The solubility of oxygen in water above 343 K has been studied in a number of investigations.[199–202] The following equation has been obtained[203] on the basis of experimental data:[199,204]

$$\ln X_2 = -54.0411 + 6889.61/T + 18.554 \ln(T/100). \quad (8)$$

The solubilities of oxygen in water at 348–573 K, calculated by Eqn. (8), are also listed in Table 1. The error of the determination of these quantities is 2%.

Table 1. The solubilities of oxygen ($10^5 X_2$, mole fraction) in water at 273.15–573.15 K (p_{O_2} = 101.325 kPa).[4,193,203]

T, K	From Eqn. (6)	From Eqn. (7)	T, K	From Eqn. (6)	From Eqn. (7)	T, K	From Eqn. (8)	T, K	From Eqn. (8)
273.15	3.949	3.958	313.15	1.867	1.874	353.15	1.478	453.15	2.038
278.15	3.460	3.465	318.15	1.773	1.778	358.15	1.462	473.15	2.388
283.15	3.070	3.075	323.15	1.697	1.697	363.15	1.450	493.15	2.852
288.15	2.756	2.761	328.15	1.635	1.631	368.15	1.445	513.15	3.460
293.15	2.501	2.508	333.15	1.586	1.575	373.15	1.444	533.15	4.250
298.15	2.293	2.301	338.15	1.549	1.530	393.15	1.487	553.15	5.276
303.15	2.122	1.982	343.15	1.521	1.493	413.15	1.599	573.15	6.603
308.15	1.982	1.991	348.15	1.502	1.463	433.15	1.780		

The solubility of oxygen in heavy water (D_2O) has been measured as a function of temperature[205] (p_{O_2} = 101.325 kPa):

T, K	278.15	283.15	288.15	293.15	298.15	303.15	308.15	313.15
$10^5 X_2$, mole fraction	3.729	3.332	2.950	2.673	2.459	2.263	2.101	2.000

The solubility of oxygen in D_2O is higher than in H_2O, but the difference diminishes with increase in temperature from 278 to 313 K.

The solubilities of different oxygen isotopes in pure water[193,194] and sea water[195] have been investigated. Heavy oxygen isotopes dissolve in water more readily than the light isotopes.

2. Minima in the temperature variation of the solubility of oxygen in water

Table 1 shows that, with increase in temperature, the solubility of oxygen diminishes to a minimum and then increases. The minimum solubility of oxygen in pure water is observed at 373 K (p_{O_2} = 101.325 kPa) and is independent of whether the water was saturated with air or oxygen.

The minima on the curves relating the solubility of gases in liquids to temperature were first observed in the study of the solubilities of hydrogen[206] and helium[207] in water. On the basis of the general rules governing the behaviour of binary mixtures, it has been pointed out[208] that there must be a minimum in the temperature variation of the solubilities of all gases in liquids.

The presence of a minimum in the temperature variations of the solubilities of gases and the thermodynamic interpretation of this phenomenon have been reported.[209] A minimum has been observed experimentally[210] in the temperature variation of the solubility of radon in water (at T_{min} = 366 K). However, the author himself[210] believed that the minimum in the solubility of radon is an anomalous phenomenon. It has been reported[211] that the minimum in the solubilities of the majority of gases in water occurs in the range 323–343 K. The minimum solubility of oxygen in water at T_{min} = 348 K (p_{O_2} = 10 MPa) has been established experimentally.[212,213] Later the inversion in the influence of temperature on the solubility of oxygen in water was confirmed,[199,200] but the values of T_{min} were found to be higher than those observed previously[212,213] by 37 K (at p_{O_2} = 7–35 atm and 70–140 atm). A minimum has been observed[214] in the influence of temperature on the solubility of oxygen in pure water at approximately 373 K (p_{O_2} = 20–60 atm). The latest studies[201,215] established the presence of a minimum in the solubility of oxygen in water at ~373 K regardless of pressure (in the range 1–5 MPa). An increase in pressure from 0.7 to 5 MPa hardly affects T_{min},[199,201] but a further increase in pressure from 7 to 10 MPa leads to a decrease in T_{min}.[216] The presence of a minimum in the plot of the solubility of oxygen in water against temperature is a firmly established fact. The explanation of this phenomenon is considered below.

3. Solubility of oxygen in water—a recommended standard in the measurements of the solubilities of gases in liquids

The solubility of oxygen in pure water at 298.15 K has been more often and more thoroughly measured than in other gas–liquid systems. After a critical analysis of the most reliable data, Battino and Clever[7] recommended as a standard the solubility of oxygen in pure water at 298.15 K and p_{O_2} = 101.325 kPa, which is characterised by the following parameters: α = 0.02847, L = 0.03108, $X_2 = 2.295 \times 10^{-5}$, and $c_w = 1.274 \times 10^{-6}$.[7] The average error in the calculation of this solubility from seven of the most reliable results is 0.21%.

Numerous data obtained by different workers for the solubility of oxygen in water over a wide temperature range have been analysed[4] and the solubilities in the range 273.15–348.15 K have been recommended with an average error of 0.30% (Table 1). The solubility of oxygen in water, amounting to $X_2 = 2.301 \times 10^{-5}$ (T = 298.15 K; p_{O_2} = 101.325 kPa, was determined in 1979 with an average error of 0.017%.[193] This solubility is greater by 0.35% than the value $X_2 = 2.295 \times 10^{-5}$ recommended by Battino and Clever.[7] The error in the measurement of the solubility of oxygen obtained by Benson et al.[193] is smaller by an order of magnitude than that of the value recommended by Battino and Clever.[7] Therefore the quantity $X_2 = 2.301 \times 10^{-5}$ may be regarded as the most reliable and the solubilities of oxygen obtained by new methods, with the aid of new types of apparatus, etc. should be compared with it.

4. The influence of the nature and concentration of electrolytes on the solubility of oxygen in water

The introduction of electrolytes into water leads as a rule to the salting out of oxygen.[40,198,217] The salting out coefficient, called in the literature the Sechenov coefficient $K_{c\alpha}$, has come to be regarded as a quantitative characteristic of this phenomenon:

$$K_{c\alpha} = 1/c \lg(\alpha_0/\alpha), \text{ [litre mol}^{-1}\text{]}, \quad (9)$$

where c is the molar concentration of the electrolyte and α_0 and α are the solubilities (expressed in terms of the Bunsen coefficients) of oxygen in pure water and in the electrolyte solution. Over a narrow range of electrolyte concentrations and for low values of the latter, Eqn. (9) holds rigorously. This concentration range depends on the nature of the electrolyte and the gas.[1,40,218–220] There exist numerous modifications of the Sechenov equation.[219,221,222] It has been shown[221] that for appreciable electrolyte concentrations it is useful to formulate Eqn. (9) as follows:

$$K_I = 1/I \lg(\alpha_0/\alpha), \text{ [litre mol}^{-1}\text{]}, \quad (10)$$

where the molar concentration of the electrolyte c has been replaced by the ionic strength I:

$$I = 1/2\sum c_i Z_i^2, \text{ [litre mol}^{-1}\text{]},$$

where c_i is the molar concentration of the ith ion and Z_i is its charge. Eqn. (10) holds for $I \leqslant 5.6$.[223]

It has been proposed[218,219] that the dependence of the logarithm of the solubility of oxygen on the electrolyte concentration over a wide range of the latter be described by the formula

$$\lg(\alpha_0/\alpha) = K_c^0 c/(1 + K_c' c), \quad (11)$$

where K_c^0 and K_c' are constants. For $c \to 0$, Eqn. (11) is converted into the Sechenov equation (9). The available literature values of the coefficients for the salting out of oxygen from solutions in 70 electrolytes, calculated with the aid of Eqn. (9) over a wide range of experimental conditions, have been compiled and tabulated.[220] In one of the latest studies,[13] the coefficients for the salting out of oxygen from solutions of 68 electrolytes at 310.2 K and p_{O_2} = 101.325 kPa were determined. In some communications, there is no information about the determination of the particular equilibrium concentration (solubility) of oxygen and the errors of the calculation of the salting out coefficients are not indicated. The corresponding data are not considered in this review. The oxygen salting out coefficients depend on the nature of the anions and cations, temperature and pressure, and for certain electrolytes also on their concentration.

(a) Solutions of acids

Coefficients for the salting out of oxygen from aqueous HCl, H_2SO_4, and HNO_3 solutions are presented in Table 2. The solubility of oxygen as a function of H_2SO_4 concentration is described by a curve with a maximum.[224] The oxygen salting out coefficients decrease with increase in the H_2SO_4 concentration.[224] An appreciable effect of pressure (in the range 0.5–1.5 MPa) on K_c has not been observed.[228] The coefficient for the salting out of oxygen from 1 M H_2SO_4 is 0.10 litre mol^{-1} (p = 5 MPa) at 323 K and hardly changes with increase in temperature to 523 K.[225] Extrema are observed in the dependence of the solubility of oxygen on the HNO_3 concentration and temperature. This will be described in detail below.

The dependence of the logarithm of the solubility of oxygen on the H_3PO_4 concentration (in the range 1.5–14.6 M) at 298–333 K is not linear.[229] The literature data[166,230,231] concerning the influence of the H_3PO_4 concentration (85–100 wt.%) and temperature (373–423 K) on the solubility of oxygen are contradictory.

Table 2. The coefficients of the salting out of oxygen from 1.0 M HCl, H_2SO_4, and HNO_3 solutions.

Acid	T, K	p_{O_2}, MPa	$K_{c\alpha}$, litre mol^{-1}	Refs.
HCl	288.15	0.1	0.044	[224]
	298.15	0.1	0.031	[224]
	310.2	0.1	0.027	[13]
H_2SO_4	288.15	0.1	0.105	[224]
	298.15	0.1	0.087	[224]
	323.15	5	0.10	[225]
HNO_3	283.15	1–6	0.0440	[226, 227]
	293.15	1–6	0.0255	[226, 227]
	303.15	1–6	0.0175	[226, 227]
	310.2	0.1	0.010±0.004	[13]
	313.15	1–6	0.0115	[226, 227]
	323.15	1–6	0.0090	[226, 227]
	333.15	1–6	0.0050	[226, 227]

Table 3. The coefficients of the salting out ($k_{c\alpha}$) of oxygen from solutions of alkalis (p_{O_2} = 101.325 kPa).

Alkali	298.15 K [40]		310.2 K [13]	
	c^*, M	$K_{c\alpha}$, litre mol^{-1}	c^*, M	$K_{c\alpha}$, litre mol^{-1}
LiOH	0–0.07	0.332	0–4.058	0.137
LiOH	0.15–1.2	0.091	—	—
NaOH	0–1.2	0.181	0–4.071	0.169
KOH	0–0.8	0.176	0–4.871	0.160
RbOH	0–0.5	0.168	0–3.187	0.161
CsOH	0–0.5	0.158	0–2.325	0.153

* c is the range of concentrations of alkalis for which $K_{c\alpha}$ has been determined.

Note. The numerals in square brackets denote references (Translator).

(b) Solutions of alkalis

The coefficients for the salting out of oxygen from solutions of alkali are presented in Table 3, which shows that two different values of $K_{c\alpha}$ are observed in LiOH solutions at 298.15 K: in the region of low (up to 0.07 M) and high (0.15–1.2 M) electrolyte concentrations. A similar effect has been established in a study of the solubility of oxygen in NaOH solutions at 323–423 K and p_{O_2} = 1–5 MPa:[232] an anomalously large oxygen salting out coefficient has been observed in 0.01–0.1 M NaOH solutions (K_c =

0.65 litre mol^{-1}). An increase in temperature from 323 to 523 K (p_{O_2} = 5 MPa) hardly affects K_c in NaOH solutions.[225] At 310.2 K, the quantity $K_{c\alpha}$ is constant over the entire concentration range (0–4.059 M) of LiOH.[13] The dependence of the solubility of oxygen on the KOH concentration is described satisfactorily by the Sechenov equation (9) over a wide range of concentrations (0–16 M) and temperatures (288–373 K).[229,233–235]

The coefficient for the salting out of oxygen from NH_4OH solution is very low (k_c = 0.006 litre mol^{-1}) and hardly changes with increase in the NH_4OH concentration (0–8 M) and temperature (323–423 K).[225]

(c) Salt solutions

Salts as a rule salt out oxygen from solutions (Tables 4–6). It is seen from Tables 4–6 that the oxygen salting out coefficients as a rule increase with decrease in the atomic number and size of the ion. For salts with the F^-, BO_2^-, and $B_4O_7^{2-}$ ions, anomalously large values of K_c have been observed.[220] Salts with H^+, NH_4^+, and Li^+ cations are exceptions (Table 6).

Table 4. The coefficients K_c (litre mol^{-1}) of the salting out of oxygen from solutions of alkali metal halide salts (T = 298.15 K, p_{O_2} = 0.1 MPa).[40]

Ion	F^-	Cl^-	Br^-	I^-
Li^+	0.725 –0.385	0.112 0.070	0.252 0.084	0.163
Na^+	0.284	0.145	0.131	0.120
K^+	0.203	0.129	0.117	0.093
Rb^+	0.146	0.120	0.104	0.086
Cs^+	0.114	0.098	0.078	0.062

Note. The concentration range was 0–1.2 M for the sodium and potassium salts and LiI and 0–0.5 M for rubidium and caesium salts. For LiF, the first value of K_c was measured in the range 0–0.01 M and the second in the range 0.04–0.1 M; for LiCl and LiBr, the first value of K_c was measured in the range 0–0.07 M and the second in the range 0.15–1.2 M.

It is noteworthy that two oxygen salting out coefficients can be observed in solutions of lithium salts: in the region of low (up to 0.7 M) electrolyte concentrations and in the region of high concentrations (0.15–1.2 M).[40] In the first concentration range, the coefficients K_c are greater by a factor of 2–3 than in the second. An analogous effect has been established for $NaHCO_3$.[232] The same [constant] value of K_c has been observed only for the salts LiI, Li_2SO_4, and Li_2CO_3 at concentrations in the range 0–1.2 M). Constant values of K_c have been established[13] for the salts LiCl, $LiNO_3$, and Li_2SO_4 over a wide concentration range (Table 6). The anomalous behaviour of lithium salts in relation to oxygen persists over a wide temperature range[217,220] and has been explained by the appreciable hydration of lithium ions, as a result of which the amount of free water diminishes markedly and this leads in its turn to a corresponding decrease in the solubility of oxygen.

It is seen from Tables 2–6 that there are differences in the salting out of oxygen by acids, alkalis, and salts. The replacement of hydrogen in acids by a metal cation results in an appreciable increase in K_c. The oxygen salting out coefficients K_c are smaller for many salts than for alkalis. Alkali metal, ammonium, *p* metal (Mg, Ca, Ba, Al) and *d* metal (Mn, Fe, Co, Ni, Cu, Zn) carbonates, phosphates, and borates hydrolyse, as a result of which different forms of the salts exist in solution and it is difficult to attribute the salting out coefficient to any particular form. The coefficients for the salting out of oxygen from solutions in these salts therefore require careful checking. An example is provided by the values of $K_{c\alpha}$ for the salting out of oxygen from NH_4Cl solutions obtained in two investigations.[12,218] The solubilities of oxygen in NH_4Cl solution established by MacArthur[218] have been included in many textbooks[11] and handbooks.[10] However, measurements in recent years have shown[12,13] that $K_{c\alpha}$ for oxygen in NH_4Cl solution is appreciably smaller ($K_{c\alpha}$ = 2.76 litre mol^{-1}) than the value obtained previously[218] ($K_{c\alpha}$ = 2.79 litre mol^{-1}). In order to prevent the hydrolysis of *p* and *d* metal salts, a small amount of acid (0.01–0.04 M), which does not affect appreciably the solubility of oxygen, was added by Lang and Zander.[13] One can therefore postulate that Lang and Zander[13] determined the values of $K_{c\alpha}$ for oxygen in the presence of non-hydrolysed salts.

Table 5. The coefficients K_c (litre mol^{-1}) of the salting out of oxygen from solutions of alkali metal salts with oxygen-containing anions at 298.15 K (p_{O_2} = 0.1 MPa).[40*]

Ion	ClO_4^-	NO^-	SO_4^{2-}	CO_3^{2-}	PO_4^{3-}
Li^+	0.218 (0–0,07 M) 0.066 (0.15–1.2 M)	0.196 (0–0.07 M) –0,040 (0.15–1.2 M)	0.244 —	0.254 —	— —
Na^+	0.160	0.124	0.376	0.464	0.652 (0–0.6 M)
K^+	0.150 (0–0,12 M)	0.105	0,297 (0–0,6 M)	0.379	0.507 (0–0.6 M)
Rb^+	0.138** (0–0.1 M)	0.096 (0–0,5 M)	0.290 (0–0,3 M)	—	—
Cs^+	—	0.066 (0–0,5 M)	0,255** (0–0.45 M)	—	—

*The salt concentration ranges for which the values of K_c were calculated are indicated in brackets; in the remaining cases the concentration range was 0–1.2 M.

**The values of K_c for the salting out of oxygen from $RbClO_4$ and Cs_2SO_4 solutions quoted by Battino et al.[4] are incorrect; the values from the original source[40] are quoted here.

The electron shells of *s*, *p*, and *d* elements have a significant influence on the values of $K_{c\alpha}$ (Fig. 2). Fig. 2 shows that $K_{c\alpha}$ for oxygen is a periodic function of the atomic number of the element in the Periodic System. The periodicity of the function is manifested by the fact that a similarity is observed between sections of the given

relation within Periods, i.e. there is a periodic variation in $K_{c\alpha}$ with increase in the atomic number of the element.

Table 6. The coefficients $K_{c\alpha}$ (litre mol^{-1}) of the salting out of oxygen from salt solutions (T = 310.2 K; p_{O_2} = 0.1 MPa).[13]

Ion	Cl^-	NO_3^-	SO_4^{2-}	HSO_4^-
Li^+	0.094 (0—3.978 M)	0.081 (0—2.869 M)	0.278 (0—1.903 M)	—
Na^+	0.131 (0—4.017 M)	0.101 (0—2.078 M)	0.334 (0—1.762 M)	0.165 (0—2.628 M)
K^+	0.124 (0—2.976 M)	0.098 (0—1.852 M)	0.331 (0—0.582 M)	0.158 (0—2.017 M)
Rb^+	0.114 (0—2.957 M)	0.095 (0—2.017 M)	0.304 (0—1.199 M)	—
Cs^+	0.099 (0—6.122 M)	0.090 (0—0.930 M)	0.295 (0—1.909 M)	—
NH_4^+	0.076 (0—3.001 M)	0.059 (0—3.120 M)	0.227 (0—3.499 M)	0.121 (0—3.010 M)
Mg^{2+}	0.202 (0—2.879 M)	0.172 (0—2.238 M)	0.280 (0—2.013 M)	—
Ca^{2+}	0.226 (0—4.477 M)	0.192 (0—1.961 M)	—	—
Ba^{2+}	0.265 (0—1.509 M)	0.223 (0—0.298 M)	—	—
Mn^{2+}	0.206 (0—2.127 M)	0.173 (0—1.936 M)	0.252 (0—1.740 M)	—
Co^{2+}	0.222 (0—1.494 M)	0.187 (0—1.487 M)	0.270 (0—1.494 M)	—
Ni^{2+}	0.214 (0—1.490 M)	0.186 (0—2.062 M)	0.271 (0—1.489 M)	—
Cu^{2+}	0.194 (0—1.517 M)	0.177 (0—1.267 M)	0.257 (0—1.000 M)	—
Zn^{2+}	0.211 (0—2.959 M)	0.181 (0—1.651 M)	0.268 (0—2.151 M)	—
Cd^{2+}	0.188 (0—2.029 M)	0.167 (0—2.046 M)	0.269 (0—3.026 M)	—
Al^{3+}	0.301 (0—2.503 M)	0.252 (0—1.095 M)	0.687 (0—0.396 M)	—
Fe^{3+}	0.219 (0—2.064 M)	0.210 (0—1.037 M)	0.438 (0—0.940 M)	—
La^{3+}	0.334 (0—2.478 M)	0.243 (0—2.227 M)	—	—
Ce^{3+}	0.347 (0—2.462 M)	0.236 (0—2.952 M)	—	—
Th^{4+}	—	0.302 (0—1.385 M)	—	—

Note. The salt concentration ranges for which the values of $K_{c\alpha}$ have been calculated are indicated in brackets; the error of the calculation of $K_{c\alpha}$ is 1—4%; the values of $K_{c\alpha}$ for the salts $ZnCl_2$ and $CdCl_2$ were calculated from the slope of the lg $\alpha - c$ curve in the salt concentration range 0—0.5 M.

(d) The influence of pH on the solubility of oxygen

We are aware of only two studies[236,237] in which the influence of pH on the solubility of oxygen in water and electrolyte solutions was investigated. Both in pure water and in 0.1 M CH_3COONa solution, the solubility of oxygen is independent of pH in the range from 2 to 12 at 293—313 K. Only when the pH is reduced from 2 to 0 and increased from 12 to 14 does the solubility of oxygen diminish, which is due to the presence of considerable amounts of HCl and NaOH respectively. The solubility of oxygen in 0.1 M Na_2SO_4 solution does not change when the pH is reduced from 6 to 1.

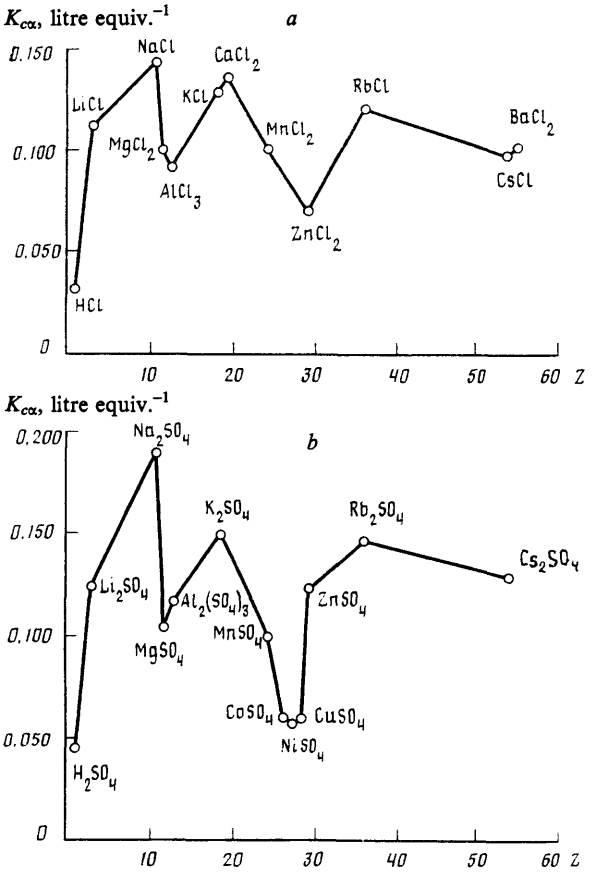


Figure 2. Dependence of the oxygen salting-out coefficient in solutions of chlorides (*a*) and sulphates (*b*) on the atomic number of the cation in the Periodic System; T = 298.15 K; p_{O_2} = 101.325 kPa (the quantities $K_{c\alpha}$ for $CoSO_4$, $NiSO_4$, and $CuSO_4$ were obtained at p_{O_2} = 5 MPa[225]).

5. The influence of temperature and pressure on the oxygen salting out coefficients

With increase in temperature, the coefficients $K_{c\alpha}$ for the salting out of oxygen from electrolyte solutions as a rule diminish.[220] The influence of temperature (in the range 298—523 K) on the values of $K_{c\alpha}$ in solutions of ammonium, copper, zinc, nickel, and cobalt sulphates and ammonium chloride is slight.[184] The temperature coefficients of the quantities $K_{c\alpha}$ depend on pressure. With increase in oxygen pressure, the coefficients for salting out from $(NH_4)_2SO_4$ solutions increase and those for salting out from NH_4OH

and $NaHCO_3$ solutions diminish.[232,238] At elevated temperatures ($T > 423$ K), the influence of pressure on the coefficients $K_{c\alpha}$ decreases. At high electrolyte concentrations (~ 0.5 M) and pressures up to 2 MPa, the coefficients $K_{c\alpha}$ diminish with increase in temperature.[232] At high temperatures ($\sim 400-428$ K) there is an inversion: with increase in temperature from 273 to 400–428 K, the coefficients $K_{c\alpha}$ diminish to a minimum and increase on subsequent increase in T (above 428 K).[202,232]

Minima in the dependence of $K_{c\alpha}$ on T are observed at temperatures exceeding by 25–50 K the temperature of the minimum solubility of oxygen in water.

6. The influence of pressure on the solubility of oxygen in electrolyte solutions

At oxygen pressures up to 3 MPa, solutions of oxygen both in water and in electrolyte solutions rigorously obey Henry's law expressed in the form applied to ideal systems.[212,229,232,239–241] The temperature and electrolyte concentration influence the behaviour of the oxygen–liquid phase systems.[201,232] At 323 K and $p_{O_2} > 3$ MPa, deviations from Henry's law are observed in dilute electrolyte solutions. With increase in electrolyte concentration, the deviations from Henry's law diminish.[232]

7. The solubility of oxygen in solutions of mixtures of electrolytes. The problem of the calculation of individual ionic oxygen salting-out coefficients

The solubility of oxygen has been investigated in solutions of mixtures of certain electrolytes.[242–248] It has been established[243–245,247] that the solubility of oxygen in solutions of mixtures of electrolytes is close to the corresponding solubility for the dominant electrolyte in the solution. However, it has been noted[248] that the salting out depends on the overall salt concentration in solution.

Solubilities of oxygen in solutions of KCl, $CaCl_2$, and $AlCl_3$ at the same equivalent concentrations and in their mixtures are the same and independent of the nature of the cation.[246] The availability of only a few and contradictory data hinders the calculation of the individual ionic oxygen salting-out coefficients and the analysis of their additivity.

We shall consider the existing literature procedures for the calculation of individual ionic oxygen salting-out coefficients. On the assumption that the salting out effect of ions and salts is additive, it has been suggested that the overall salting out effect be described with the aid of the formula:[249,250]

$$\lg (c_0/c) = \sum h_i I_i ,$$

or:[12]

$$\lg (c_0/c) = \sum K_i m_i, \qquad (12)$$

where h_i are constants referring to salts or ions, I_i are the contributions of ions of the *ith* kind to the ionic strength of the solution, K_i are individual ionic salting-out coefficients, and m_i are the molalities of the ith components (in the ionic or molecular form).

It has been suggested[251] that the salting-out coefficient be regarded as the sum of three constants characterising the behaviour of the gas (K_g), the cation (K_c) and the anion (K_a):

$$K = K_g + K_c + K_a, \qquad (13)$$

where K_g is the component of the gas salting-out coefficient independent of the nature of the electrolyte in the solution of which the gas is being dissolved and which depends solely on temperature, while K_c and K_a are the components of the salting-out coefficient referring to the cations and anions which are independent of temperature.

Van Krevelen and Hoftijzer[251] failed to give a theoretical justification of Eqn. (13) and did not indicate a method for the determination of the quantities K_g, K_c, and K_a although the values of K_c and K_a for 13 ions are quoted (Table 1). The assumption of the additivity of the salting-out coefficient underlies Eqn. (13).

The authors[251] assumed arbitrarily (without explanation) that $K_{H^+} = K_{NO_3^-} = 0$. It may be that the authors assumed that the coefficient for the salting out of oxygen from HNO_3 solutions at 298 K is lowest (Table 2). Lang and Zander[13] calculated the individual ionic oxygen salting-out coefficients on the assumption that $K_{Na^+} = 0$ (Table 7). The Na^+ ion was selected as the reference ion on the grounds that the Na_2SO_4 molecules are more effectively dissociated than H_2SO_4.

The idea of subdividing the gas salting-out coefficient into three components [see Eqn. (13)] was used by a number of workers[223,250,252] who obtained individual ionic oxygen salting-out coefficients (Table 7) from the experimental coefficients for the salting out of oxygen from electrolyte solutions by the method of least squares (i.e. by minimising the squares of the differences between the experimental K_c and the values of K_c calculated from the ionic salting-out coefficients K_i). These coefficients have been related[12] to the Sechenov constant by means of Eqn. (12), while other investigators[13,250,252] used for this purpose the equation:

$$K_{c\alpha} = 1/2 \sum_i K_i n_i Z_i^2,$$

where n_i is the number of ions of the ith kind referred to one electrolyte molecule and Z_i is the ionic charge.

For the same ions, the individual ionic salting-out coefficients, obtained by different workers, are not identical owing to the differences between the reference systems and between the methods of calculation of the ionic salting-out coefficients adopted. In order to eliminate the differences between the relative reference systems, a single reference system has been proposed.[253] It makes it possible to recalculate the ionic salting-out coefficients with the aid of the formulae

$$K_c^* = K_c - K^+, \qquad (14)$$

$$K_a^* = K_a - K^-, \qquad (15)$$

$$K_g^* = K_g + K^+ + K^-, \qquad (16)$$

and thus to compare the individual ionic oxygen salting-out coefficients obtained by different workers. In Eqns. (14)–(16), K_c and K_a, and K_g are the individual salting-out coefficients calculated by the method of least squares[223,250] or by some other procedure from the experimental values of K_c and K^+ and K^- are arbitrary constants referring to the cation and anion respectively. On adding together Eqns. (14)–(16), we obtain

$$K = K_c^* + K_a^* + K_g^*.$$

The new values of K_i^*, characterising the behaviour of the gas (K_g^*), the cation (K_c^*), and the anion (K_a^*), are evidently equivalent to the values of K_g, K_c, and K_a respectively in Eqn. (13), since the summation of the former three quantities (K_i^*) leads to the same value of K as the summation of the latter three quantities (K_i).

The NaCl solution–O_2 system, for which $K_c = K_c^*(Na^*) = 0.091$ and $K_a = K_a^*(Cl^-) = 0.021$ and which has been most thoroughly investigated, has been proposed as the reference system.[253]

Table 7. The ionic oxygen salting-out coefficients at 298.15 K.

Cation	Ionic salting-out coefficients (litre mol^{-1}) from different sources						Anion	Ionic salting-out coefficients (litre mol^{-1}) from different sources					
	[251]	[249]	[223]	[12]	[2]	[13]*		[251]	[249]	[223]	[12]	[250]	[13]*
H^+	0	0.000	−0.1110	0	−0.774	−0.200	F^-	—	—	—	—	0.982	—
Li^+	—	—	−0.0416	—	−0.664	−0.060	Cl^-	0.021	0.021	0.3416	0.029	0.844	0—257
Na^+	0.094	0.091	−0.0183	0.107	−0.550	−0.000	Br^-	0.011	0.012	0.3310	—	0.820	—
K^+	0.071	0.074	−0.0362	0.099	−0.596	−0.013	I^-	0.005	—	0.3124	—	0.821	—
Rb^+	—	—	−0.0449	—	−0.662	−0.025	OH^-	0.061	0.066	0.3875	0.081	0.941	0.340
Cs^+	—	—	−0.0584	—	−0.666	−0.041	NO_3^-	0	−0.001	0.3230	0.013	0.802	0.220
NH_4^+	0.031	0.028	−0.0737	0.033	−0.720	−0.098	ClO_4^-	—	—	—	—	0.888	—
NEt_4^+	—	—	—	—	−0.912	—	CNS^-	—	—	0.2612	—	—	—
Mg^{2+}	0.046	0.051	−0.0568	0.119	−0.314	−0.025	HSO_3^-	—	—	0.3869	—	—	—
Ca^{2+}	0.051	0.053	−0.0547	—	−0.303	−0.015	HSO_4^-	—	—	—	0.069	—	0.333
Ba^{2+}	0.060	—	−0.0473	—	−0.297	0.003	HS^-	—	—	0.3718	—	—	—
Mn^{2+}	0.046	—	−0.0625	—	−0.311	−0.029	HCO_3^-	—	—	—	0.083	—	—
Cd^{2+}	—	—	−0.0062	—	—	−0.031	SO_4^{2-}	0.021	0.022	0.3446	0.121	0.453	0.163
Zn^{2+}	0.046	0.048	−0.0590	0.108	—	−0.024	CO_3^{2-}	0.021	0.021	0.3754	—	0.485	—
Sr^{2+}	—	—	−0.0445	—	—	—	SO_3^{2-}	—	—	0.3275	—	—	—
Fe^{2+}	0.049	—	−0.0602	—	—	—	PO_4^{3-}	—	—	0.3265	—	0.320	—
Co^{2+}	0.058	—	−0.0534	—	—	−0.021							
Ni^{2+}	0.059	—	−0.0520	—	—	−0.022							
Cu^{2+}	—	—	—	—	—	−0.030							
Al^{3+}	—	—	−0.0986	—	—	−0.018							
Fe^{3+}	—	—	—	—	—	−0.032							
La^{3+}	—	—	—	—	—	−0.014							
Ce^{3+}	—	—	—	—	—	−0.015							
Th^{4+}	—	—	—	—	—	−0.017							

*At 313.15 K.

Note. The numerals in square brackets denote references (Translator).

However, a subsequent check[254] of the proposed method indicated considerable discrepancies between the ionic salting-out coefficients obtained by different workers.[12,250]

A satisfactory agreement has been established[12,223,250,252] between the experimental and calculated (assuming additivity) coefficients for the salting out of oxygen from aqueous and non-aqueous solutions of certain electrolytes. However, analysis of the oxygen salting-out coefficients based on additivity using individual ionic salting-out coefficients[12,223,250] with the aid of the constant differences law showed[254] that additivity is by no means observed in all cases. The best agreement between the experimental oxygen salting-out coefficients and the values calculated assuming additivity has been observed for nitrates, sulphates, chlorides, bromides, hydroxides, and perchlorates. Considerable discrepancies have been observed between K_{exp} and K_{calc} for fluorides, lithium salts, and lithium hydroxides, ammonium hydroxide, carbonates, and phosphates.[254] These discrepancies may be caused by the unreliability of the experimental coefficients for the salting out of oxygen from certain electrolyte solutions, the possibility of complex formation (lithium salts), and the hydrolysis of many salts (carbonates and phosphates).

V. Extrema in the influence of temperature and electrolyte concentration on the solubility of oxygen

In most modern textbooks of chemistry and physical chemistry and also in the Short Chemical Encyclopaedia and in certain monographs,[255,259] it has been reported that either all gases dissolve in liquids with evolution of heat and that the solubility of gases in liquids diminishes as the temperature is raised or that there are rare exceptions where the solubility of a gas at normal pressures increases with increase in temperature.

However, experimental facts have shown that the inversion of the influence of temperature and electrolyte concentration on the solubility of oxygen and other non-polar gases in water and electrolyte solutions is not all that rare a phenomenon. Experimental data are available concerning the presence of a minimum in the temperature variation of the solubility of oxygen not only in water[199,201,202] but also in organic and inorganic solvents,[260–262] in electrolyte solutions,[212,217,225,227] and in natural salt solutions.[202,215]

Measurements of the solubility of oxygen in pure water over a wide range of temperatures and pressures carried out most thoroughly during the last ten years have shown that the temperature of the minimum solubility of oxygen in pure water is 373 K (p_{O_2} = 0.1–5 MPa).[201,202] It is seen from Table 8 that in aqueous electrolyte solutions this temperature is lower and depends on the nature and concentration of the electrolyte (Figs. 3 and 4).[217,226,227] An increase in the electrolyte concentration shifts the region of the solubility minimum towards lower temperatures. The depth of the minimum also diminishes under these conditions. An increase in pressure from 1 to 5 MPa hardly affects the temperature of the minimum solubility of oxygen in the electrolyte solution but increases the depth of the minimum.[232]

Thus the presence of a minimum in the temperature variation of the solubility of oxygen in water and in electrolyte solutions should be regarded as a firmly established fact. The practical importance of this phenomenon is that it can be used in the development of rational conditions for the deoxygenation of sewage and industrial waters, i.e. for the deaeration process at the temperature of the minimum solubility of oxygen, for the selection of the conditions for the autoclave dissolution of sulphide products, in processes designed to protect power station equipment against oxygen, etc.[214,263]

Table 8. Experimental quantities characterising the minima in the temperature variations of the solubility of oxygen in water and aqueous electrolyte solutions.

Electrolyte	c, M	p, MPa	T_{min}, K	Refs.
H_2O		10	348	[212]
		10	348	[213]
		0.7—3.5	385	[199]
		7—14	385	[200]
		2—6	373	[214]
		1—5	373	[201]
		4.3—5.2	373	[202, 215]
KCl	0.5—2.0	10	348	[212]
NaOH	0.5—4.0	10	348	[213]
NaOH	1.0—1.5	5	373	[225]
NaOH	0.01—0.1	1—5	373	[232]
NH_4OH	2.87—8.28	5	373	[225]
KOH	0.92—16.2	0.1	373	[235]
H_2SO_4	0.5—1.5	5	373	[225]
HNO_3	8	1—6	333	[227]
HNO_3	10	1—6	323	[227]
$(NH_4)_2SO_4$	0.75—3.0	5	373	[225]
$CuSO_4$	0.5—1.5	5	373	[225]
$CoSO_4$	0.5—1.5	5	373	[225]
$NiSO_4$	0.5—1.5	5	373	[225]
$NaHCO_3$	0.1—0.5	1—5	373	[232]
$NaNO_3$	0.1—1	1—5	373	[232]
NaCl	0.85	4.3—5.2	373	[202, 215]
NaCl	2.78	4.3—5.2	353	[202, 215]
NaCl	5.09	4.3—5.2	333	[202, 215]
NaCl	1.0*	0.1	348	[217]
Na_2SO_4	1.0*	0.1	338	[217]
LiCl	1.0*	0.1	336	[217]
Li_2SO_4	0.95*	0.1	333	[217]

*Molal concentrations.

1. The salting in of oxygen by aqueous electrolyte solutions

The salting out of oxygen is characteristic of many electrolytes over a wide range of experimental conditions.[220] However, in many instances salting in takes place.[40,238,264] The salting in phenomenon has been observed for a number of electrolytes both at 298 K (LiF, $NiNO_3$,[40] HNO_3,[226,227] $Na_2B_4O_7$,[165] and tetraethylammonium bromide[264]) and at higher temperatures of ~333—423 K (LiCl, $NaBO_2$, $Na_2B_4O_7$,[220] NH_4OH,[238] HNO_3,[226,239] H_3PO_4 [231]). The salting in of oxygen in the presence of salts is observed in the range of low concentrations of the latter where most of the water is not bound to the electrolyte ions. On the other hand, for acids and alkalis salting in is observed at high electrolyte concentrations.[227,231,265] The salting in of oxygen in dilute $Na_2B_4O_7$ solutions has been explained by the formation of oxygen-borate complexes.[165]

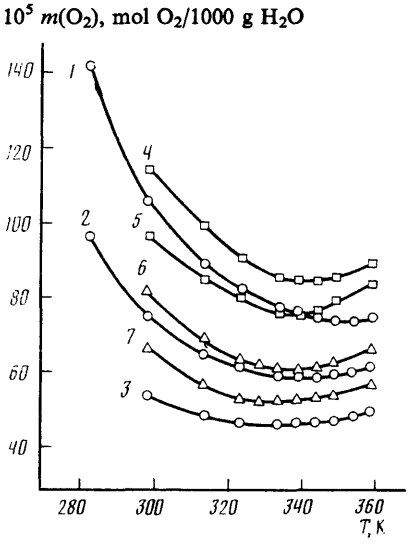


Figure 3. Temperature dependence of the solubility of oxygen in aqueous solutions of Na_2SO_4 (curves *1*—*3*), LiCl (curves *4* and *5*), and Li_2SO_4 (curves *6* and *7*) at different molalities *m*: *1* and *4*, 0.2; *2* and *6*, 0.6; *3* and *5*, 1.0; *7*, 0.95.[217]

The increase in the solubility of oxygen in HNO_3 with increase in temperature has been attributed to the decomposition of HNO_3:[266]

$$2HNO_3 \rightleftarrows N_2O_4 + H_2O + {}^1/_2O_2.$$

Apparently the inversion in the influence of the electrolyte concentration on the solubility of oxygen is associated both with the characteristics of the dissociation of electrolytes and with the formation of oxygen complexes and the structural changes occurring in solutions.

2. Theoretical justification of the inversion in the influence of temperature on the solubility of oxygen

The first explanation of the minima on the curves relating the solubilities of gases in liquids to temperature is due to Winkler.[267] On the basis of the relation between the absorption of a gas and the internal friction (viscosity) and density of the liquid, he showed that the changes in the latter two properties as a function of temperature affect the solubility of the gas in opposite ways, which leads to a minimum in the temperature variation of the solubility of the gas in the liquid.

According to Kuenen,[208] the minimum in the temperature variations of the solubilities of gases in liquids is due to the fact that, above the critical temperature of the solvent, both components mix in all proportions, i.e., as the critical point is approached, an increase in solubility should be observed. Therefore in cases where

the solubility of the gas diminishes with increase in temperature, the minimum solubility should occur at a higher temperature. Consequently the existence of a minimum is a common phenomenon and is not associated with specific properties of the solvent and the dissolved gas.

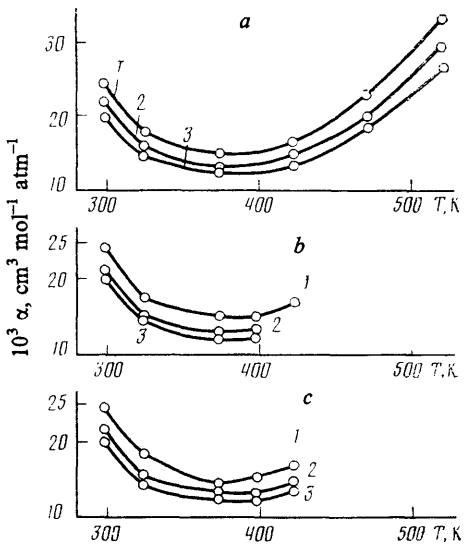


Figure 4. Temperature dependence of the solubility of oxygen in solutions of $CuSO_4$ (*a*), $CoSO_4$ (*b*), and $NiSO_4$ (*c*) at different salt concentrations (M): *1*, 0.5; *2*, 1.0; *3*, 1.5.[225]

The next attempt to explain the presence of a minimum in the curves for the temperature variation of the solubilities of gases in water was made by Tammann[211] in 1926 on the basis of the hydration theory. However, the gas solubility minima are encountered also in non-aqueous solvents.[260–262]

According to modern ideas,[268,269] there are two mechanisms of the dissolution of a gas in water and in aqueous electrolyte solutions: the filling of vacancies and the substitution of water molecules in the structural framework of water. These two mechanisms have been called vacancy and solvation mechanisms by Borina and Samoilov,[268] the insertion and insertion-substitution mechanisms by Frank and Quist,[270] and the hydrophobic and hydrophilic mechanisms by Krestov.[271] The diminution of the vacancy contribution and the increase in that of the solvation contribution with increase in temperature are responsible for the presence of a minimum in the curves for the temperature variation of the solubility of oxygen (as well as other non-polar gases in water).[268]

The phenomenon of inversion in the influence of temperature on the solubility and the salting-out coefficients of oxygen in water and in electrolyte solutions can be understood in the light of the thermodynamic theory[272–274] and with the aid of the structural model of solutions of non-polar gases in water.[272,275] The presence of a minimum in the curves for the temperature variation of the solubility of oxygen implies that the dissolution is exothermic at $T < T_{min}$ and endothermic at $T > T_{min}$. On the assumption that the ice-like framework is stabilised in the vicinity of the gas molecule, the minimum in the temperature variation of the solubility of a gas has been explained[272] with the aid of thermodynamic analysis. The partial molar enthalpy of solution of the gas was expressed in the form

$$\bar{H}_2 = \bar{H}_2^0 + \Delta\bar{H}^0\left(\frac{\partial\nu}{\partial y}\right)_p - \overline{H}_2^\circ + H_2^{st},$$

where $\overline{H}_2^\circ$ is the partial enthalpy of gas molecules in solution subject to the exclusion of the structural contribution corresponding to the redistribution of the molecules between the vacancies and the framework, $\Delta\overline{H}^\circ$ is the enthalpy of the transfer of one mole of water from the cavities in the water structure to the framework, ν is the fraction of water molecules at the lattice sites of the framework, and $y = N_2/N_1$, N_1 and N_2 being the numbers of water and gas molecules in the system. The structural component H_2^{st} diminishes with increase in temperature, because $\Delta\overline{H}^\circ$, defined by the formula

$$\left(\frac{\partial\nu}{\partial y}\right)_p = \nu(1-\nu)[\nu - 2(1-\nu)]\cdot\frac{\Delta\bar{H}^0}{RT^2},$$

decreases with increase in temperature. The structural component of the hydrophobic hydration of a gas diminishes with increase in temperature, while the exothermic component of the transfer of molecules from the vacancies in the water structure to the framework disappears, as a result of which the overall heat of solution of gases becomes positive.

A method has been proposed[276] for the determination of the temperature of the minimum solubility of a gas in a liquid. For this purpose, the relation between the standard thermodynamic characteristics calculated from the solubility (ΔH_2°) and in terms of the phase distribution constant ($\Delta H_2^\ominus$) is expressed in the form

$$\Delta H_2^\ominus = \Delta H_2^\circ - \Delta H_{cond,1}^\circ, \qquad (17)$$

where $\Delta H_{cond,1}^\circ$ is the standard enthalpy of condensation of the solvent under a pressure p_1.

In contrast to the generally adopted approach in the study of the dissolution of a gas in a liquid (G⇄S), Krestov and Kudryavtsev[276] suggested that account be taken of the composition of the vapour phase, i.e., that the dissolution should be described by G + V⇄S, where G, V, and S are respectively the symbols for the gas, the vapour, and the solvent in the solution.

Since at the temperature of the minimum solubility of the gas $\Delta H_2^\circ = 0$, Eqn. (17) becomes:

$$\Delta H_2^\ominus = -\Delta H_{cond,1}^\circ,$$

The point of intersection of the $\Delta H_2^\ominus(T)$ and $\Delta H_{cond,1}^\circ(T)$ relations defines the temperature of the minimum solubility of the gas.

The experimental data show that the temperature dependence of the oxygen salting-out coefficient is also described by a curve with a minimum.[215,232] In the literature attempts have been made[274] to establish the causes of the inversion in the influence of temperature on the coefficients for the salting-out of non-polar gases from aqueous electrolyte solutions.

The temperature dependence of the coefficient of the salting out of a gas from aqueous solutions has been found:

$$\left(\frac{\partial K_{c\alpha}}{\partial T}\right)_p = \frac{H_1 - H_1^*}{2{,}3\,mRT^2} = \frac{\partial\lg(f_1^*/f_1^0)}{\partial T}, \qquad (18)$$

where H_1 and H_1^* are the enthalpies of water molecules in water and in solution, f_1^* and f_1° are the fugacities of water over the solution and pure water, and m is the molal electrolyte concentration. The

experimental vapour pressures of water over electrolyte solutions show that the differences $H_1 - H_1^* > 0$ and increase with temperature. In conformity with Eqn. (18), the quantities $K_{c\alpha}$ should increase more rapidly with temperature at high values of the latter.[274] However, it is not stated[274] why $K_{c\alpha}$ decreases with increase in temperature at low values of the latter.

On combining the Gibbs–Helmholtz equation and the Sechenov equation, one can obtain

$$\frac{\partial K_{c\alpha}}{\partial T} = \frac{(H_2)_{H_2O} - (H_2)_{soln}}{2.3\, mRT^2} = \frac{1000}{m\rho} \frac{\partial \lg (f_2/f_2^0)}{\partial T} - K_{c\alpha} \frac{\partial \ln \rho}{\partial T},$$

where $(H_2)_{H_2O}$ and $(H_2)_{soln}$ are the enthalpies of dissolved oxygen molecules in pure water and in solution respectively, ρ is the density of the solution, and f_2^0 and f_2 are the fugacities of dissolved oxygen in pure water and in solution.

Apparenty both the appearance of a minimum on the curves relating the solubility of oxygen to temperature and the minimum in the temperature dependence of $K_{c\alpha}$ are caused by the structural changes in the solution, i.e. the quasi-clathrate (vacancy) and quasi-crystalline (solvation) structures of the oxygen solution predominate at low and high temperatures respectively. The temperature-dependent differences in the nature of the oxygen dissolution process are caused by the different relative enthalpies of dissolved oxygen in water and in the solution, which leads to a minimum on the curves for the temperature variation of the salting-out coefficient.

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The great role of oxygen in many chemical, biochemical, electrochemical, ecological, and corrosion processes has made it necessary to know its solubility in water and in electrolyte solutions. This requires in turn the existence of precise, highly sensitive and convenient methods for the determination of the concentration of dissolved oxygen. Electrochemical methods, in particular membrane voltammetric sensors, which make it possible to measure the concentration of dissolved oxygen in various gas–liquid systems over a wide range of experimental conditions, have come to be most widely used during the last five years. However, the smallest error (less than 0.1%) can be achieved with the aid of the volumetric method.

Despite the large number of methods of expressing the solubility of oxygen, preference has been given at the present time to the Henry coefficient (K_H) and the mole fraction (X_2).

The solubility of oxygen in water is the recommended standard quantity in the measurements of the solubilities of gases in liquids.

Temperature and the nature and concentration of the electrolytes exert a significant influence on the solubility of oxygen in water. The problem of the individual ionic oxygen salting-out coefficients has been discussed for the first time.

The greatest advances have been made in the study of the influence of temperature and the nature and concentration of electrolytes on the solubility of oxygen. Such studies have led to the discovery of extrema involving a change in the sign of the temperature variation of the solubility of oxygen in water and in electrolyte solutions and also a change from salting out to salting in (or conversely) with increase in the concentrations of certain electrolytes and temperature.

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