OZONE TRANSFER FROM GAS INTO WATER AND CONTACT EQUIPMENT DESIGN

Andrzej K. Biń
Faculty of Chemical and Process Engineering, Warsaw University of Technology, Warsaw, Poland

Keywords: ozone, mass transfer, chemical reaction, contact equipment design

Summary

Theoretical background of ozone mass transfer from gas into water has been discussed in detail. This discussion is preceded by presenting ozone physical and chemical properties. Much attention has been devoted to the methods of the volumetric mass transfer coefficients \( k_{L_a} \) as well as the mass transfer coefficients \( k_L \) determination and predictions. Special emphasis has been put on listing the more recent references presenting experimental data on ozone contactors and designs, aiming at greater effectiveness of the transferred ozone. Comparison of ozone contactors performance has been made, indicating the major factors that can be considered during final selection of the ozonation equipment. In a separate section mass transfer with chemical reactions has briefly been described. Simple examples of mass (ozone) balance in ozone contactors have been given. Some emphasis has been put on disinfection process carried out using ozone. Final section briefly summarizes design principles of ozone contactors.

1. Introduction

Vast majority of the ozone technical applications concerns its activity within the liquid phase, and historically the earliest one was the treatment of drinking water. In this case it has mainly been used for disinfection purposes and because of its supreme ability in inactivation of microorganisms that ozone usage has still remained an important step in drinking water treatment. Ozone, when applied in purification of drinking water, allows to limit chlorine dose in the final stage of the treatment process thus enabling to meet
the regulations for the residual chlorine concentration in the fresh water (< 10 μg/L) as well as to reduce generation of harmful chloroorganic compounds – disinfection by-products – DBPs, e.g. such as trihalomethanes (THM). On the other hand ozone dissolved in the treated raw water may undergo numerous chemical reactions that could lead to other undesired by-products such as bromates. According to the EPA regulations, effective since January 1, 2002, the maximum concentration limits (MCL) of the most relevant DBPs should be maintained as follows: bromates - 10 μg/L; chlorites - 1 mg/L; THMs – 80 μg/L and haloacetic acids – 10 μg/L. This means that ozone introduction during the drinking water treatment should carefully be controlled in order to eliminate or to reduce DBPs level as much as possible.

Ozone belongs to the strongest oxidants and this chemical property enables to apply it in oxidizing toxic or undesired pollutants that are present in different wastewaters. In this case ozone may be used as a single oxidant or in combination with other oxidizing agents such as hydrogen peroxide or UV irradiation promoting generation of chemically very effective hydroxyl radicals. Using the combined oxidizing agents leads to the so-called advanced oxidation processes (AOPs), discussed in a separate chapter.

In general, since ozone is expected to act within the liquid (mainly aqueous) phase, it should effectively be introduced there from the gaseous phase. Hence, ozone transfer from the gas phase into the liquid one and dissolution there corresponds to that widely known as the absorption process. Therefore, design of ozone transfer from gas into water should be discussed based on the principles and rules that govern the effective absorption process. Possibly high effectiveness of the ozone absorption process (> 90%) is required since ozone generation is accomplished by direct using of electric energy (typically corona discharge process) and residual (unabsorbed) ozone must not be released to the atmosphere (environmental and health issues).

2. Ozone Properties

2.1. Main Physical and Chemical Properties

Under the normal conditions ozone is a gas of specific odor resembling sulfur dioxide or chlorine. At very small concentrations in air its smell is even freshly pleasant; however, at higher concentrations its smell is strong and pungent. Ozone is a colorless gas at low concentrations and is blue at high concentrations or in the liquid state. Crystals of solid ozone are violet. At any state ozone is very sensitive on sudden changes of pressure or shakes since they may induce its explosive decomposition.

The molecule of ozone is formed by three atoms of oxygen, O₃, shaping an isosceles triangle with a top angle equal to 116°49’ and the length of oxygen-oxygen bonds ca. 128 pm. The structure of the ozone molecule can be described as a resonance hybrid of four canonical forms having a bipolar character (cf. Figure 1).

The basic state of the ozone molecule can be treated as a two-radical singlet, however, the molecule has electrophilic character since the electrons remain paired maintaining continuous dipole character between the limiting structures.
Main ozone physical and chemical properties are listed in Table 1. The temperature dependences for some of them are shown in Figures 2 – 5.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular mass</td>
<td>47.9982 g mol⁻¹</td>
<td>Gas density (273 K; 1.01 bar)</td>
<td>2.142 kg m⁻³</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(293 K; 1.01 bar)</td>
<td>1.996 kg m⁻³</td>
</tr>
<tr>
<td>Normal boiling point</td>
<td>161.2 K</td>
<td>Liquid density (90 K)</td>
<td>1574 kg m⁻³</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(161.2 K)</td>
<td>1352 kg m⁻³</td>
</tr>
<tr>
<td>Melting point</td>
<td>80.7 K</td>
<td>Solid density (77.2 K)</td>
<td>1728 kg m⁻³</td>
</tr>
<tr>
<td>Critical temperature</td>
<td>261.05 K</td>
<td>Molar heat of vaporization (161.2 K)</td>
<td>13.88 kJ mol⁻¹</td>
</tr>
<tr>
<td>Critical pressure</td>
<td>55.7 bar</td>
<td>Gas heat capacity (273 K)</td>
<td>38.1 J mol⁻¹ K⁻¹</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(293 K)</td>
<td>39.1 J mol⁻¹ K⁻¹</td>
</tr>
<tr>
<td>Critical density</td>
<td>0.539 kg dm⁻³</td>
<td>Liquid heat capacity (90 - 128 K)</td>
<td>90.4 J mol⁻¹ K⁻¹</td>
</tr>
<tr>
<td>Critical volume</td>
<td>89 cm³ mol⁻¹</td>
<td>Liquid viscosity (161.2 K)</td>
<td>0.272 mPa s</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(90.2 K)</td>
<td>1.56 mPa s</td>
</tr>
<tr>
<td>Critical compressibility factor</td>
<td>0.228</td>
<td>Surface tension (77.7 K)</td>
<td>43.8 mN m⁻¹</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(90.2 K)</td>
<td>38.4 mN m⁻¹</td>
</tr>
<tr>
<td>Acentric factor</td>
<td>0.210</td>
<td>Dielectric constant (90.2 K)</td>
<td>4.75</td>
</tr>
<tr>
<td>Redox potential (298 K, pH=0)</td>
<td>2.07 V</td>
<td>Dipole momentum of gas</td>
<td>0.58 D</td>
</tr>
<tr>
<td>Extinction coefficient</td>
<td>3300⁻¹(254 nm) dm³ mol⁻¹ cm⁻³</td>
<td>Magnetic properties</td>
<td>diamagnetic</td>
</tr>
<tr>
<td></td>
<td>3150⁻¹(258 nm) dm³ mol⁻¹ cm⁻¹</td>
<td>gas</td>
<td>paramagnetic</td>
</tr>
<tr>
<td></td>
<td></td>
<td>liquid</td>
<td>paramagnetic</td>
</tr>
<tr>
<td></td>
<td></td>
<td>solid</td>
<td></td>
</tr>
</tbody>
</table>

Table 1. Selected properties of ozone.

Two sets of ozone diffusivity in water are shown in Figure 5. The more recent ones published by Johnson and Davies (1996) most likely are more accurate. The earlier data measured by Matrozov et al. (1976) are lower by 23 % when compared with the results of Johnson and Davies (1996). The commonly applied Wilke and Chang correlation is plotted in Figure 5 using the molar liquid volume of ozone at the normal boiling point $V_L = 35.52$ cm³ mol⁻¹. In this case the mean error in predicting ozone diffusivity in water from the Wilke and Chang correlation equals 6 % for the temperature range of 10 to 50°C. For comparison an approximation of the data on oxygen diffusivity in water is
also plotted in this figure. It is interesting that the ratio of diffusivities of these species in water decreases with increasing temperature. The ratio $\frac{D_{O_2-H_2O_2}}{D_{O_2-H_2O_2}}$ changes from 0.795 at 20°C to 0.706 at 50°C.

Figure 2. Dependence of ozone saturated vapor pressure on temperature.

Figure 3. Dependence of ozone molar density on temperature.
More detailed discussion on ozone solubility in liquids and its decomposition in natural waters is presented in the next two paragraphs.

2.2. Ozone Solubility in Liquids

The data on solubility of gases in liquids are of great theoretical and practical interest. In modeling processes that involve dissolution (absorption) of gases in liquids such data are of primary importance. In general, gas solubility in liquids represents a special case of the phase equilibria between the gas and liquid phases where the gaseous component is either above its critical temperature or has a vapor pressure above 1.013 bar at the system temperature. The other component will exist as a liquid and is referred to as solvent. There are different ways in expressing gas solubility in liquids. Those derived...
from the Henry’s law and most frequently applicable are as follows (subscript $A$ denotes a species being absorbed or desorbed):

$$p_A = He_A x_A$$  \hspace{1cm} (1)$$

$$p_A = He^*_A C_{LA}$$  \hspace{1cm} (2)$$

$$C_{GA} = H_A C_{LA} = \frac{1}{S} C_{LA}$$  \hspace{1cm} (3)$$

Interrelations among these definitions of gas solubility are available elsewhere (Biń, 2006).

More recent compilation of the available data on ozone solubility in liquids has been published by Biń (2006). Most of them refer to water and aqueous solutions of inorganic compounds (salts and acids). Very little information can be found on ozone solubility in organic liquids (solvents). Typically, the data due to different authors are very scattered and differ considerably when compared each other. The reasons of such a situation on one hand can be attributed to ozone decomposition in the aqueous environment, and on the other – to the applied experimental techniques as well as to the experimental data treatment. Published experimental data on the dimensionless Henry’s law constant vs. temperature are presented in Figure 6.

![Graph](image.png)

Figure 6. Dependence of the dimensionless Henry’s law constant on temperature in the system ozone-water.
In aqueous solutions containing salts under the same conditions (temperature, ozone partial pressure) ozone solubility will be lowered compared to that observed in “pure” solvent (water), in accord to the familiar “salting-out effect”. In practice this effect can be quantified by means of the Sechenov expression commonly applied for electrolyte solutions of low concentration:

\[
\log \left( \frac{H_{el}}{H_0} \right) = \log \left( \frac{\alpha_0}{\alpha_{el}} \right) = K, C_s = \sum h_i I_i \quad (4)
\]

The expression contains ion-specific salting-out constants \((h_i)\) while salt concentration is accounted for by the ionic strength if the individual ion \(I_i\). More detailed information on the salting-out effect on ozone solubility in aqueous solutions can be found elsewhere (Biń, 2006).

### 2.3. Ozone Decomposition in Natural Waters

Ozone spontaneously decomposes in aqueous environment by a complex mechanism that involves generation of free radicals of which hydroxyl radicals play a key role. In general in aqueous solutions ozone can react by either direct mode (involving molecular ozone) or by indirect mode involving chain radical reactions leading to the oxidation products of the substrates present in the water. The direct reaction of aqueous ozone is relatively slow while the reactions with hydroxyl radicals are very fast. Much research effort has been devoted in studying ozone decomposition mechanism in the aqueous environment. From the experimental investigations two major models have been suggested: the SBH model developed by the Swiss authors (Staehelin and Hoigné, 1982; Bühler et al., 1984; Staehelin et al., 1984; Staehelin and Hoigné, 1985) and the TFG model (Tomiyasu et al., 1985). In both these models complex free radical chain reactions have been assumed, with the following steps taken into account: initiation, propagation and termination. The models differ mainly in details at the initiation step and in propagation step by the assumed presence of the radicals \(\text{HO}_3^-\) and \(\text{HO}_4^-\) as well as in reactions with the ozonide radical \(\text{O}_3^-\) treated as a chain transmitter in the radical reactions.

Based on the assumed possible mechanisms a theoretical (mechanistic) approach of ozone decay in the waters has been attempted by some authors with rather limited success (cf. for example Viridis, 1995; Westerhoff et al., 1997; Nemes et al., 2000; Beltrán, 2004; Kumar and Bose, 2004, Tiwari and Bose, 2006). This is mainly caused by the fact that it is quite difficult to establish a possibly complete set of the relevant reactions and to know or to estimate the necessary kinetics rate constants. Typically a large number of reactions should be taken into account and the resulting stiff set of differential equations is difficult for solving. A solution is eventually obtained by comparing it and/or fitting to the experimental data (decay curves). Following the developing experimental technique mechanistic models of ozone decomposition are continuously modified and improved (cf. papers by Bezbarua and Reckhow, 2004; Buffle et al., 2006; Kim et al., 2007b).
In natural waters which contain a variety of chemical compounds ozone will react with the various organic (e.g., NOM – natural organic matter) or inorganic (e.g., Fe²⁺, Mn²⁺) species resulting in further decomposition and formation of secondary oxidants (e.g., HO⁺).

Ozone demands are associated with a number of factors such as:

- Reactions with NOM (oxidation of NOM leads to formation aldehydes, organic acids, and aldo- and ketoacids).
- Organic oxidation byproducts. As a result they can become more biodegradable giving rise to BDOC (biodegradable dissolved carbon) or AOC (assimilable organic carbon).
- Synthetic organic compounds (SOC) which can eventually be oxidized or even mineralized under favorable conditions. Organic compounds (pollutants) such as phenols, pesticides, polyaromatic hydrocarbons (PAH), pharmaceuticals etc. belong to this category.
- Oxidation of bromide ion resulting in formation of hypobromous acid, hypobromite ion, bromate ion, brominated organics and bromamines.
- Bicarbonate or carbonate ions (measured as alkalinity) which will scavenge the hydroxyl radicals and form carbonate radicals.

The decay of ozone in natural waters is characterized by a fast initial decrease of ozone concentration in the liquid phase (frequently called instantaneous ozone demand), followed by a second stage in which ozone concentration decrease can be approximated by the first-order kinetics (Park et al., 2001; Von Gunten, 2003; Gujer and von Gunten, 2003). The half-life of ozone depends on the water quality and may range from seconds to hours. The stability of aqueous ozone depends on the water matrix, especially on its pH, the type of NOM and on its alkalinity (Hoigné, 1998).

For practical purposes the global kinetics of ozone decay in the aqueous environment has been approximated with different expressions. The following two are among the most frequently quoted:

\[-\frac{d[O_3]}{d\tau} = k_A [O_3]^m [OH^-]^n\]  \hspace{1cm} (5)

\[-\frac{d[O_3]}{d\tau} = k_A [O_3]^m + k_B [OH^-]^n [O_3]^p\]  \hspace{1cm} (6)

The values of the powers exponents depend on pH of the aqueous environment and its matrix – first of all on the substances or ions that act as scavengers of free radicals. The kinetics constants depend on the temperature and could be approximated by the Arrhenius type equations (Hewes and Davison, 1971; Miyahara et al., 1974; Sullivan and Roth, 1980; Sotelo et al., 1987; De Smedt, 2000; Hsu et al., 2002).

Quite often the first-order kinetics of ozone decay has been assumed (e.g. Qiu, 1999; Chen et al., 2001; Gujer and von Gunten, 2003; Park et al., 2004; Kuosa et al., 2005; Rosal et al., 2006; López-López et al. 2007):
While the first-order rate constant, $k_D$, is dependent upon temperature and pH of the water (cf. Figure 7). In spite significant scatter of the experimental data shown in Figure 7 it can be concluded that for pH < 6 (acidic conditions) the first-order kinetics constant of ozone decomposition is of the order of $10^{-4}$ s$^{-1}$. Hence, under acidic conditions (pH < 3) hydroxyl ions will not affect the rate of ozone decomposition and Eqs. (5) and (6) will simplify to Eq. (7).

![Figure 7](image-url)

Figure 7. Dependence of the first-order rate constant of ozone decay, $k_D$, on pH at (a) 20°C; and (b) 25°C; 1) Morioka et al. (1991); 2) Eq. (6) with $k_A = 3, n = 0.5, k_B = 45, m = 1$
Some authors proposed empirical expressions for the first-order rate constant, $k_D$, describing ozone decomposition in the natural waters (cf. Von Gunten and Laplanche, 2000). These expressions contain the main water parameters such as pH, TOC, alkalinity and UV$_{254}$. They represent a reasonable approximation for the real natural waters and may be used in preliminary designing stage of the ozonation step.

Ozone decomposition in the aqueous environment may depend on the presence of specific pollutants. For example, Pi et al. (2005) studied the effect of aromatic solutes and concluded that when present at several μM concentrations they can strongly accelerate ozone decomposition rate. They explained it by formation of the intermediate product (hydrogen peroxide) and proposed a new reaction pathway of ozone decomposition.

Recently, Mizuno et al. (2007a, b) carried out carefully planned experiments on ozone self-decomposition in water within the range of temperatures of 15 to 30°C and pH-values from 2.7 to 7.8. From their experiments they concluded that ozone self-decomposition follows the second-order kinetics with respect to dissolved ozone concentration and approximated their data with an empirical expression similar to Eq. (5) giving the following relationship for $k_A$ and the power exponents in this equation:

$$k_A = 37.4 \exp \left( \frac{13367 \pm 1589}{T} \left( \frac{T - 293}{293} \right) \right); \quad n = 2, \text{ and } m = 0.73.$$  

They found that inorganic carbon affects ozone self-decomposition in water. At higher concentrations of inorganic carbon the rate of ozone self-decomposition in water decreased. The authors explained this by scavenging effects of inorganic species on hydroxyl radicals. Furthermore, they developed a radical model of ozone self-decomposition based on considerations of 22 possible reactions and managed to obtain good agreement with their own experimental data within the indicated range of temperature and pH values. They concluded that their model should be applicable for engineering design of the ozonation process.

From their studies on the effects of temperature, pH, water alkalinity as well as the type and concentration of DOC, Elovitz et al. (1999, 2000) introduced a concept of $R_{ct}$ parameter which determines a ratio between the concentrations of the hydroxyl radicals and ozone in the natural water and is equal to the ratio of hydroxyl and ozone doses expressed by the time integrals measured during the batch experiments using samples of the water in question.

$$R_{ct} = \frac{[\text{OH}^*]}{[O_3]} = \frac{\int [\text{OH}^*] \, d\tau}{\int [O_3] \, d\tau}$$  

(8)

The $R_{ct}$ parameter is coupled with a test (probe) ozone resistant-substance concentration changes with the experimental time (e.g. $p$-chlorobenzoic acid) according to the following equation
\[ \ln \left( \frac{[pCBA]}{[pCBA]_0} \right) = -k_{OH^\cdot pCBA} R_c \int [O_3] \, d\tau \]  

(9)

If Eq. (9) is fulfilled a linear plot of the experimental data points is expected using the coordinates \( \ln \left( \frac{[pCBA]}{[pCBA]_0} \right), \int [O_3] \, d\tau \). From the of such a plot a value of the \( R_c \) parameter can be found provided the value of the rate constant \( k_{OH^\cdot pCBA} \) is known. The values of the \( R_c \) parameter are typically of the order of \( 10^{-8} \) and depend on the experimental conditions. The \( R_c \) parameter reflects the concentration level of hydroxyl radicals in the ozonated water.

Apart of the above briefly discussed effects of different parameters that characterize the water matrix other factors may affect the fate (decomposition and/or reaction) of dissolved ozone in the liquid phase. Here the following factors can be mentioned:

- hydrogen peroxide (situation encountered in the AOPs),
- UV irradiation (situation encountered in the AOPs),
- presence of catalysts (including solid catalysts → catalytic ozonation),
- presence of microorganisms (when ozone is applied as disinfectant),
- solid surfaces (e.g. when ozone is applied to clean solid surfaces → electronic manufacturing).

Detailed discussion of all the above listed factors on ozone decomposition is beyond the scope of the present chapter. The book of Beltrán (2004) can here be recommended for further reading.

Bibliography


References


Biographical Sketch

**Andrzej K. Biń**, was born in Warsaw, Poland, in January 24, 1941. He graduated from the Warsaw University of Technology in 1963 as chemical engineer. His scientific career began in October, 1963, at the Chemical Department of the Warsaw University of Technology, where in 1971 he obtained the Ph.D. degree based on a thesis on air entrainment by plunging liquid jets, then in 1986 at the same University he was granted D.Sc. degree based on a series of papers on mass transfer into turbulent liquid free surfaces. During this period of time he held positions of assistant professor, then associate professor, and in 1995 he was appointed as full professor at the Faculty of Chemical Engineering of the Warsaw University of Technology. His major area of interest and scientific activity is devoted to hydrodynamics and mass transfer in multiphase systems, with special emphasis put on aeration, ozonation, advanced oxidation processes and their applications in environmental protection (water and wastewater treatment). He is a member of the International Ozone Association since 1993, in which he was elected as a Board Member and International Director. He published ca. 170 papers.