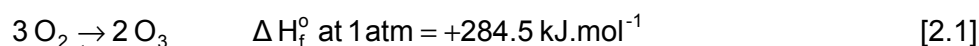

2. The Ozone

Ozone was first acknowledged in 1840 by the German chemist C.F. SCHONBEIN (1799-1868), who determined that the odor produced during sparking was caused by an unknown compound that he called ozone, from the Greek *ozein* (to smell). But it was not until twenty years later that the new substance was revealed to be a triatomic allotrope of oxygen: in 1856 Thomas Andrews showed that the ozone was formed only by oxygen, and in 1863 Soret established the relationship between oxygen and ozone by finding that *three volumes of oxygen produce two volumes of ozone*.

Formation of ozone is endothermic (2.1):



Ozone is thermodynamically unstable and spontaneously reverts back into oxygen.

Ozone is a strong oxidizing agent, capable of participating in many chemical reactions with inorganic and organic substances. Commercially, ozone has been applied as a chemical reagent in synthesis, used for potable water purification, as a disinfectant in sewage treatment, and for the bleaching of natural fibers (Ullmann's, 1991).

2.1. Physical properties of ozone

Ozone is an irritating pale blue gas, heavier than the air, very reactive and unstable, which cannot be stored and transported, so it has to be generated "in situ". It is explosive and toxic, even at low concentrations. In the Earth's stratosphere, it occurs naturally (with concentrations between 5 and 10 ppm), protecting the planet and its inhabitants by absorbing ultraviolet radiation of wavelength 290-320 nm (Ullmann's, 1991)

By analysis of the electronic structure, the molecule is considered to have the following resonant structure (see Figure 2.1):

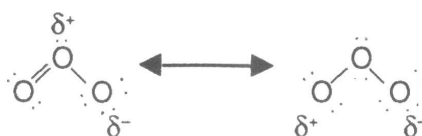


Figure 2.1. Resonant structure of ozone (Langlais et al., 1991)

characterized by end oxygen atoms with only six electrons. This fact defines the electrophilic nature that ozone shows in most of its chemical reactions.

Ozone is soluble in many substances, forming either stable or metastable solutions. Under practicable conditions in water, ozone is about 14 times more soluble than oxygen but forms a metastable solution. The stability is influenced by the presence of sensitizing impurities, such as heavy-metal cations and metal oxides, and by temperature and pressure: generally, an increase of the pressure or decrease of the temperature enhances the solubility of ozone in the aqueous phase. Most of the solubility determinations have been performed with dilute ozone, and the values extrapolated to 100% ozone. Table 2.1 lists the solubility of 100% ozone in pure water, for the range of 0-60°C.

Table 2.1. Solubility of ozone in water (Ullmann's, 1991)

Temperature (°C)	Solubility (kg.m ⁻³)
0	1.09
10	0.78
20	0.57
30	0.40
40	0.27
50	0.19
60	0.14

Some other physical properties of ozone are as follows (see Table 2.2):

2.2. Chemistry of ozone

The chemistry of ozone is largely governed by its strongly electrophilic nature. Table 2.3 compares the oxidation potential of ozone with other strong oxidizing agents.

Table 2.2. Physical properties of ozone (Ullmann's, 1991)

Physical property	Value
Molecular weight	48.0
Boiling point (101 kPa)	-111.9
Melting point	-192.7
Critical temperature	-12.1
Critical pressure	5.53 MPa
Density, gas (0°C, 101 kPa)	2.144 kg.m ⁻³
Density, liquid (-112°C)	1358 kg.m ⁻³
Surface tension (-183°C)	3.84 x 10 ⁻² N.mm ⁻¹
Viscosity, liquid (-183°C)	1.57 x 10 ⁻³ Pa.s
Heat capacity, liquid (-183 to -145°C)	1884 J.kg ⁻¹ .K ⁻¹
Heat capacity, gas (25°C)	818 J.kg ⁻¹ .K ⁻¹
Heat of vaporization	15.2 kJ.mol ⁻¹

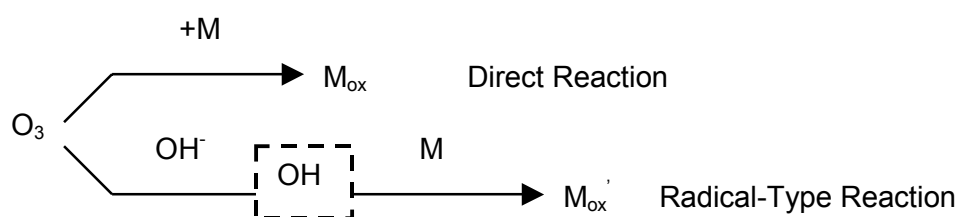
Table 2.3. Relative oxidation potentials (Ullmann's, 1991)

Species	Oxidation Potential, eV
Fluorine	3.06
Hydroxyl radical	2.80
Nascent oxygen	2.42
Ozone	2.07
Hydrogen peroxide	1.77
Perhydroxyl radical	1.70
Hypochlorous acid	1.49
Chlorine	1.36

In an aqueous solution, ozone may act on various compounds (M) in the following two ways (Hoigné and Bader, 1977a, 1977b, 1978):

- by direct reaction with the molecular ozone, and
- by indirect reaction with the radical species that are formed when ozone decomposes in water.

The two basic reactions of ozone in water are illustrated in Figure 2.2.

**Figure 2.2. Reactivity of ozone in aqueous solution (Langlais et al., 1991)**

2.2.1. Molecular ozone reactivity

The extreme forms of resonance structures in ozone molecules have been shown in Figure 2.1. This structure illustrates that the ozone molecule will act as a dipole, as an electrophilic agent, and as a nucleophilic agent.

Cyclo addition (Criegee mechanism). As a result of its dipolar structure, the ozone molecule may lead to 1-3 dipolar cyclo addition on unsaturated bonds, with the formation of primary ozonide (I) corresponding to the following reaction (Figure 2.3):

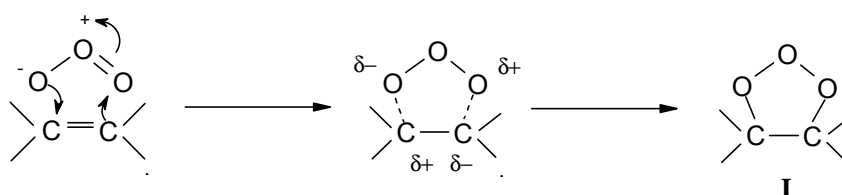


Figure 2.3. Dipolar cyclo addition of ozone on unsaturated bonds

In a protonic solvent such as water, this primary ozonide decomposes into a carbonyl compound (aldehyde or ketone) and a zwitterion (II) that quickly leads to a hydroxy-hydroperoxide (III) stage that, in turn, decomposes into a carbonyl compound and hydrogen peroxide (see the following reactions).

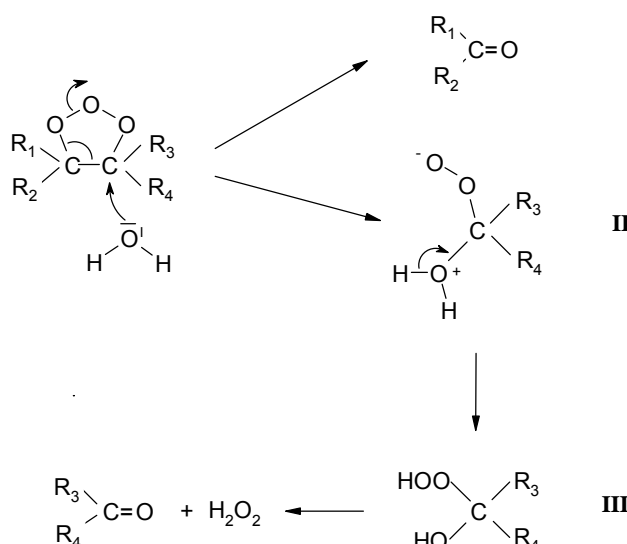


Figure 2.4. Criegee mechanism (2)

Electrophilic reaction. The electrophilic reaction is restricted to molecular sites with a strong electronic density and, in particular, certain aromatic compounds. Aromatics substituted with electron donor groups (OH, NH₂, and similar compounds) show high electronic densities on carbons located in the ortho and para positions, and so are highly reactive with ozone at these positions. On the contrary, the aromatics substituted with electron-withdrawing groups (-COOH, -NO₂) are weakly ozone reactive. In this case, the initial attack of the ozone molecule takes place mainly on the least deactivated meta position. The result of this reactivity is that the aromatic compounds bearing the electron donor groups D (for example, phenol and aniline) react quickly with the ozone. This reaction is schematically represented as follows:

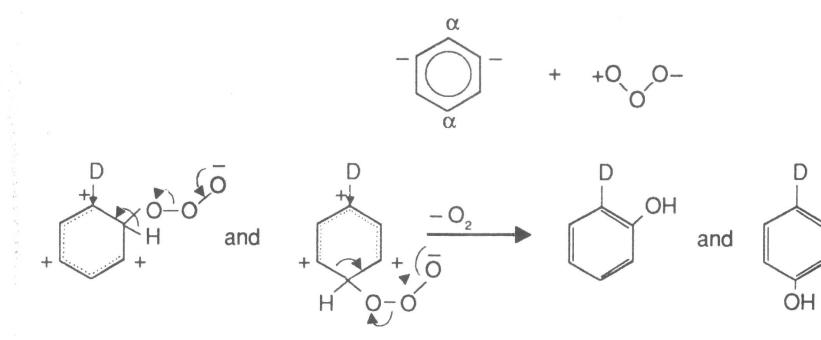


Figure 2.5. Electrophilic reaction of ozone with aromatic compounds (Langlais et al, 1991)

This initial attack of the ozone molecule leads first to the formation of ortho- and para-dihydroxylated by-products. These hydroxylated compounds are highly susceptible to further ozonation. The compounds lead to the formation of quinoid and, due to the opening of the aromatic cycle, to the formation of aliphatic products with carbonyl and carboxyl functions.

Nucleophilic reaction. The nucleophilic reaction is found locally on molecular sites showing an electronic deficit and, more frequently, on carbons carrying electron-withdrawing groups.

In summary, the molecular ozone reactions are extremely selective and limited to unsaturated aromatic and aliphatic compounds as well as to specific functional groups. In Figure 2.6 some of the organic groups capable of attack by ozone are shown:

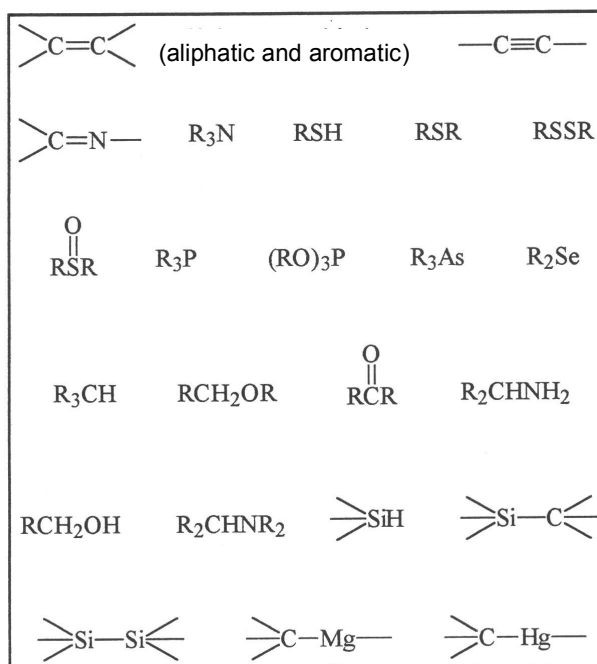


Figure 2.6. Organic groups open to attack by ozone (Rice, 1997)

Figure 2.7 diagrams the general reaction of ozonation of aromatics:

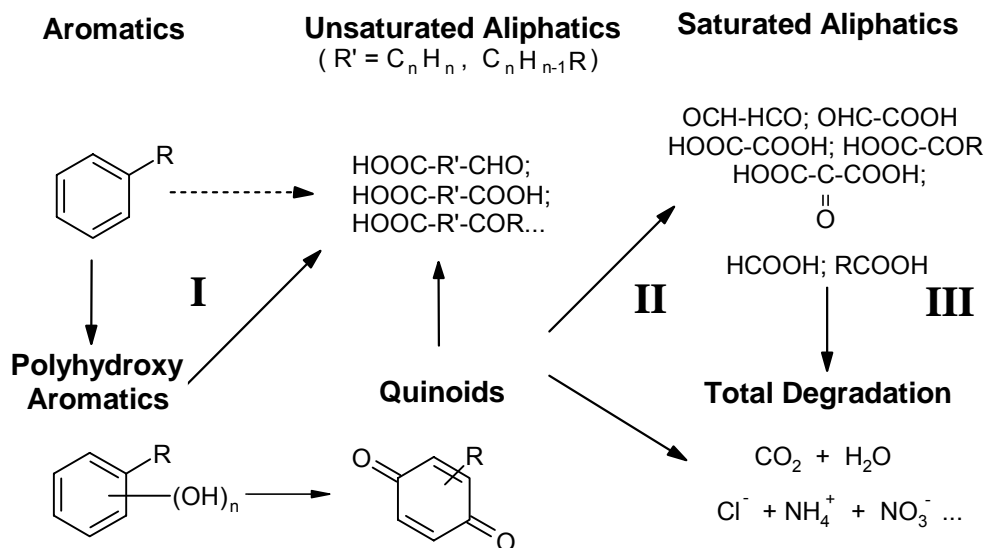


Figure 2.7. Scheme of ozonation of aromatic compounds (Langlais et al., 1991)

2.2.2. Decomposition of ozone

The stability of dissolved ozone is readily affected by pH, ultraviolet light, ozone concentration, and the concentration of radical scavengers. The decomposition rate,

measured in the presence of excess radical scavengers, which prevent secondary reactions, is expressed by a pseudo first-order kinetic equation of the following configuration:

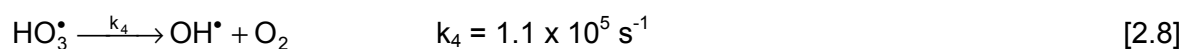
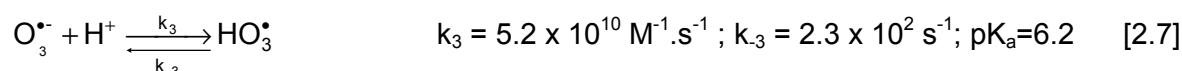
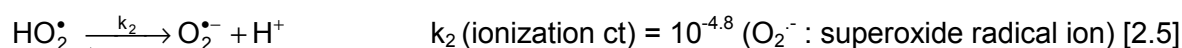
$$-\left(\frac{d[O_3]}{dt}\right)_{pH} = k' [O_3] \quad [2.2]$$

where k' = pseudo first-order rate constant for a given pH value. It is a linear function of pH (Staehelin and Hoigné, 1982). This evolution reflects the fact that the ozone decomposition rate is first order with respect to both ozone and hydroxide ions, resulting in an overall equation of the following form:

$$-\left(\frac{d[O_3]}{dt}\right)_{pH} = k [O_3][OH^-] \quad [2.3]$$

Where $k = k'/[OH^-]$.

Ozone decomposition occurs in a chain process that can be represented by the following fundamental reactions, based on the two most important models (Staehelin et al., 1984; Tomiyasu et al., 1985), including initiation step [2.4-2.5], propagation steps [2.6-2.10], and break in chain reaction steps [2.11-2.15]



The overall pattern of the ozone decomposition mechanism is shown in Figure 2.8. The first fundamental element in the reaction diagram and in the rate constant values is that the free-radical initiating step constitutes the rate-determining step in the reaction. The second is that the regeneration of the superoxide radical ion O_2^- , or its protonic form HO_2 , from the hydroxyl radical OH implies that 1 mol of ozone is consumed. As a result, all the species capable of consuming hydroxyl radicals without regenerating the superoxide radical ion will produce a stabilizing effect on the ozone molecule in water.

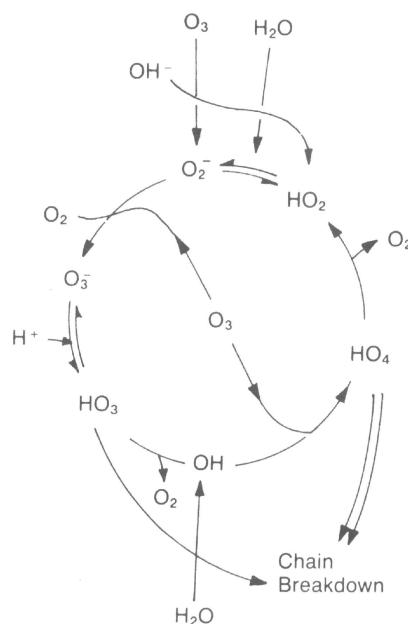


Figure 2.8. Ozone decomposition mechanism (Langlais et al., 1991)

Initiators, promoters and inhibitors of free-radical reactions. There is a wide variety of compounds able to initiate, promote, or inhibit the chain-reaction processes (Hoigné and Bader, 1977a; Staehelin and Hoigné, 1983). For Hoigné and co-workers, the initiators, promoters and inhibitors are defined in Figure 2.9.

1. *Initiators.* The initiators of the free-radical reaction are those compounds capable of inducing the formation of superoxide ion O_2^- from an ozone molecule. Those are inorganic compounds (hydroxyl ions OH^- , hydroperoxide ions HO_2^- and some cations), organic compounds (glyoxylic acid, formic acid, humic substances,...) and UV radiation at 253.7 nm.
2. *Promoters.* Promoters of the free-radical reaction are all organic and inorganic molecules capable of regenerating the O_2^- superoxide (which can promote the decomposition of ozone) anion from the hydroxyl radical. Common promoters

that are also organics include aryl groups, formic acid, glyoxylic acid, primary alcohols and humic acids. Among the inorganic compounds, phosphate species are worth special mention.

3. *Inhibitors*. The inhibitors of the free-radical reaction are compounds capable of consuming OH radicals without regenerating the superoxide anion O_2^- . Some of the more common inhibitors include bicarbonate and carbonate ions, alkyl groups, tertiary alcohols (e.g. *t*-butanol) and humic substances.

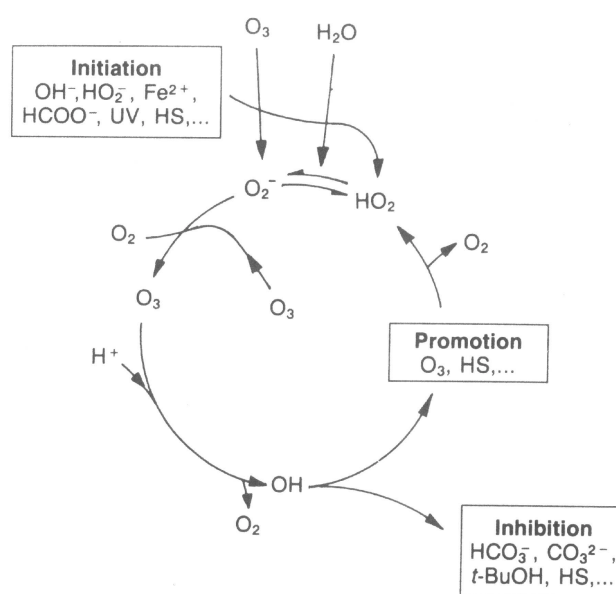


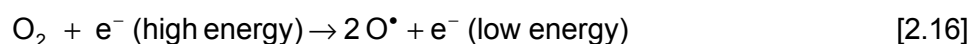
Figure 2.9. Mechanism of ozone decomposition – Initiation, promotion and inhibition of radical-type chain reaction

2.3. Generation of ozone

Ozone dissolved in liquid oxygen up to 30 percent by weight is relatively safe, while spontaneous explosions occur at more than 72 percent by weight ozone in liquid oxygen. Ozone has a tendency to separate and concentrate during evaporation due to the higher volatility of oxygen. When this occurs, the composition becomes unavoidably explosive. Conservation of ozone in liquefied freons has been attempted, but application of the process to water treatment is a problem (L'Air Liquide, French Patent, 1,246,273). Also, ozone decomposes even when dissolved in a liquefied matrix. Consequently, in water treatment, ozone must be generated on-site.

In 1857, von Siemens developed the first industrial ozone generator, which was based on corona discharges. Two concentric glass tubes were used; the outer tube was covered externally by a layer of tin, and the inner tube was covered internally by a layer of tin. Air was circulated through the annular space. This technology was later improved by the addition of circulating cooling fluids along the discharge air or oxygen gap, resulting in lower generation temperatures and less thermal destruction of the ozone.

The generation of ozone involves the intermediate formation of atomic oxygen radicals (eq. 2.16), which can react with molecular oxygen (eq. 2.17).



All processes that can dissociate molecular oxygen into oxygen radicals are potential ozone generation reactions. Energy sources that make this action possible are electrons or photon quantum energy. Electrons can be used from high-voltage sources in the silent corona discharge, from chemonuclear sources, and from electrolytic processes. Suitable photon quantum energy includes UV light of wavelengths lower than 200 nm and γ -rays.

2.3.1. Photochemical ozone generation

The formation of ozone from oxygen exposed to UV light at 140-190 nm was first reported by Lenard in 1900 and fully assessed by Goldstein in 1903. It was soon recognized that the active wavelengths for technical generation are below 200 nm. The method has been reviewed more recently in an overview by Du Ron (1982) and in state-of-the-art papers (Dohan and Masschelein, 1987). In view of present technologies with mercury-based UV-emission lamps, the 254-nm wavelength is transmitted along with the 185-nm wavelength, and photolysis of ozone is simultaneous with its generation. Moreover, the relative emission intensity is 5 to 10 times higher at 254 nm compared to the 185-nm wavelength.

Attempts to reach a suitable photostationary state of ozone formation with mercury lamps have failed (Dohan and Masschelein, 1987). The main reason for this failure is that thermal decomposition is concomitant with ozone formation. Except for small-scale uses or synergic effects, the UV-ozone process (the UV-photochemical generation of ozone) has not reached maturity. Important phases requiring additional development include the development of new lamp technologies with less aging and higher emission intensity at wavelengths lower than 200 nm (Langlais et al., 1991).

2.3.2. Electrolytic ozone generation

Electrolytic generation of ozone has historical importance because synthetic ozone was first discovered by Schönbein in 1840 by the electrolysis of sulfuric acid. The simplicity of the equipment can make this process attractive for small-scale users or users in remote areas.

Many potential advantages are associated with electrolytic generation, including the use of low-voltage DC current, no feed gas preparation, reduced equipment size, possible generation of ozone at high concentrations, and generation in the water, eliminating the ozone-to-water contacting processes. Problems and drawbacks of the method include: corrosion and erosion of the electrodes, thermal overloading due to anodic over-voltage and high current densities, need for special electrolytes or water with low conductivity, and with the in-site generation process, incrustations and deposits are formed on the electrodes, and production of free chlorine is inherent to the process when chloride ions are present in the water or the electrolyte used (Langlais et al., 1991).

2.3.3. Radiochemical ozone generation

High-energy irradiation of oxygen by radioactive rays can promote the formation of ozone. The best information on the feasibility of cheminuclear ozone generation for water treatment results from the Brookhaven project (Steinberg and Beller, 1970). Even with the favorable thermodynamic yield of the process and the interesting use of waste fission isotopes, the cheminuclear ozone generation process has not yet become a significant application in water or waste water treatment. This fact is due to its complicated process requirements.

2.3.4. Ozone generation by corona discharge (Langlais et al., 1991)

Corona discharge in a dry process gas containing oxygen is presently the most widely used method of ozone generation for water treatment. A classical production line is composed of the following units: gas source (compressors or liquefied gas), dust filters, gas dryers, ozone generators, contacting units, and off gas destruction.

It is of utmost importance that a dry process gas is applied to the corona discharge. Limiting nitric acid formation is also important in order to protect the generators and to increase the efficiency of the generation process. In normal operation of properly designed systems, a maximum of 3 to 5 g nitric acid is obtained per kilogram ozone produced with air. If increased amounts of water vapor are present, larger quantities of

nitrogen oxides are formed when spark discharges occur. Also, hydroxyl radicals are formed that combine with oxygen radicals and also ozone. Both reactions reduce the ozone generation efficiency. Consequently, the dryness of the process gas is of relevant importance to obtain a yield of ozone. Moreover, with air, nitrogen oxides can form nitric acid, which can cause corrosion. The presence of organic impurities in the feed gas should be avoided, including impurities arising from engine exhaust, leakages in cooling groups, or leakages in electrode cooling systems.

The formation of ozone through electrical discharge in a process gas is based on the nonhomogeneous corona discharge in air or oxygen. There are numerous distributed microdischarges by which the ozone is effectively generated. It appears that each individual microdischarge lasts only several nanoseconds, lasting about 2.5 to 3 times longer in air than in oxygen. The current density ranges between 100 and 1000 A.cm⁻².

By using oxygen or enriching the process air in oxygen, the generating capacity of a given ozone generator can be increased by a factor ranging from 1.7 to 2.5 versus the production capacity with air, depending on the design parameters (for example, gas discharge gap and current frequency). The nominal design capacity at which operation can be performed on a permanent basis must be considered to be at least 20 to 30 percent. The yield obtained when using an oxygen-enriched process gas is increased with a smaller gas space and an increased electrical current frequency. Since all variations result in energy loss in the form of heat, cooling of the process gas is very important. The most efficient form of cooling is the “both-side” cooling system, which is a system that has cooling on both the high-voltage side and on the ground side. However, in case of accidental breakage of the dielectric, the cooling liquid (for example, water) enters the discharge gap and causes short-circuiting of the entire system. Therefore, cooling only the ground side is the safer design.

2.4. Ozone gas transfer

2.4.1. Transfer of ozone to water without chemical reaction.

The transfer of ozone to water without reaction is currently accepted as occurring according to the double-film model (see Figure 2.10). The driving force is $(C_L^* - C_L)$. The experimental determination of the film coefficients k_L and k_G is very difficult. When the equilibrium distribution between the two phases is linear, over-all coefficients, which are more easily experimentally determined, can be used. Over-all coefficients can

be defined from the standpoint of either the liquid phase or gas phase. Each coefficient is based on a calculated over-all driving force, defined as the difference between the bulk concentration of one phase (C_L or C_G) and the equilibrium concentration (C_L^* or C_G^*) corresponding to the bulk concentration of the other phase. When the controlling resistance is in the liquid phase, the over-all mass transfer coefficient $K_L a$ is generally used:

$$m = k_G a (C_G - C_{Gi}) = k_L a (C_L - C_{Li}) = K_L a (C_L^* - C_L) \quad [2.18]$$

where m is the specific mass transfer rate. This simplifies the calculation in that the concentration gradients in the film and the resulting concentrations at the interface (C_{Li} or C_{Gi}) need not to be known. In this equation, a is the specific exchange surface in the liquid film and depends on practical conditions, such as agitation, pressure, and total gas and liquid volumes. Measuring this area is very difficult, and this is overcome by lumping it together with the over-all mass transfer coefficient. The most reliable value of k_L for ozone is in the order $2\text{-}3 \times 10^{-3} \text{ m}\cdot\text{s}^{-1}$, which is about 2.5 times lower than for oxygen (Mallevalle et al., 1975).

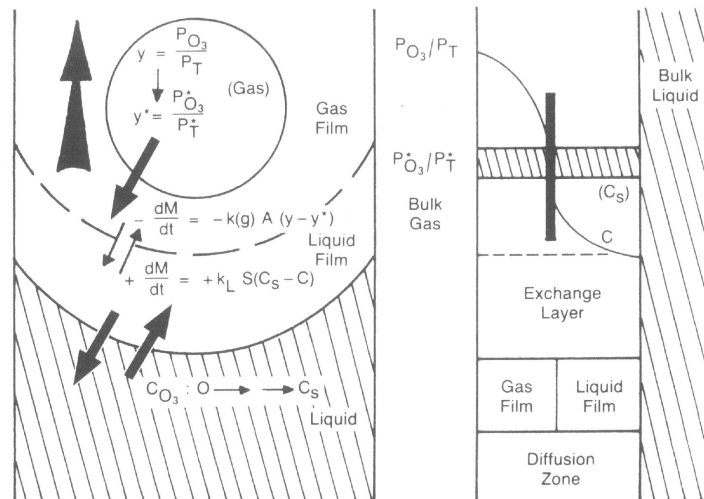


Figure 2.10. Schematic of double-film transfer (Masschelein, 1982)

2.4.2. Absorption with chemical reaction.

If the ozone transferred to the liquid is consumed by a chemical reaction, the specific transfer coefficient k_L is no longer influenced by only the diffusivity, since a significant part of the ozone dissolved in the liquid phase is exhausted continuously. Therefore,

$$k_L(R) > k_L \text{ and } (k_L(R)/k_L) = B$$

where $k_L(R)$ is the transfer coefficient in the presence of chemical reactions. The degree of enhancement depends upon the relative concentration of reacting compounds in each phase, their solubility, and relative resistance of the mass transfer and reaction steps. An approximation for B is given by Danckwerts :

$$B = \left[1 + (D_{O_3} k_1)/k_L\right]^{1/2} \quad [2.19]$$

B is an acceleration coefficient, often called enhancement factor (E), for ozone transfer, while k_1 is the first-order rate constant of the oxidation and D_{O_3} is the diffusion coefficient.

If the reaction is very fast, for example, oxidation of a solution of iodide ion at $k_1 \sim 10^4 \text{ s}^{-1}$, the oxidation takes place only at the bubble surface and no ozone is transferred into the bulk of the liquid phase ($B \sim 2.3$). For a k_1 value of 10^2 s^{-1} , which is in the range of easily oxidized organic compounds of concentrations of $0.1\text{-}0.2 \text{ mol.L}^{-1}$, B is still about 1.2. For $k_1 = 1 \text{ s}^{-1}$ and slower, the direct effect of reacting dissolved compounds on the gas transfer can be neglected and the reaction is that of pre-dissolved ozone.

2.4.3. Competitive inhibition effects in ozone-transfer-controlled reactions.

In ozone “gas-transfer controlled reaction rates”, the reaction kinetics observed, for example, those in a bubble column, are often of apparent zero order. Compounds that do not react with ozone in similar conditions can interfere by competitive inhibition mechanisms.

2.5. Toxicology and Occupational Health.

It is worthy to mention the toxic character of ozone, specially at high concentrations. While ozone is considered to be a toxic gas, there are factors which mitigate the immediate danger to individuals working with it. Toxicity is dependent on concentration and length of exposure. Figure 2.11 illustrates the relationship between various exposure levels and exposure time for humans. An exposure of less than 0.2 mg.m^{-3} can be tolerated indefinitely, 2 mg.m^{-3} (1 ppm) can be tolerated for 8 min, and up to 8 mg.m^{-3} (4 ppm) can be tolerated for one minute without producing the symptoms of coughing, eye watering, and irritation of the nasal passages. The ACGIH has set a TLV as ceiling of 0.2 mg.m^{-3} (0.1 ppm) for ozone. Equivalent parameters, called VLA (Valor Límite Ambiental), have been established in Spain, depending on the type of work. The VLA-ED

values (equivalent to TLV-TWA) are: 0.05 ppm (0.1 mg.m^{-3}) for heavy work, 0.08 ppm (0.16 mg.m^{-3}) for moderate work, 0.1 ppm (0.2 mg.m^{-3}) for light work and 0.2 ppm (0.4 mg.m^{-3}) for times of exposure lower than 2 hours.

There are other factors which lessen the risk to personnel working with ozone. The odor threshold concentration for ozone is ca. $0.02\text{-}0.04 \text{ mg.m}^{-3}$ ($0.01\text{-}0.02 \text{ ppm}$). Thus, ozone is generally detected by personnel before dangerous concentrations are reached. Moreover, once a critical concentration is reached, the results are not immediately toxic but merely symptomatic.

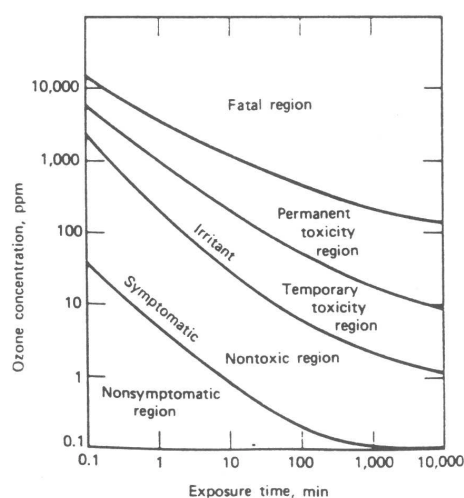


Figure 2.11. Human toxicity limits for ozone exposure

Another point of concern is the effect of ozone on drinking water. The chemistry of ozone in aqueous solution and the health effects are complex. It is clear that ozone reacts with products in the water supply (for example, humic acids) to form numerous disinfection by-products. However, the general pattern that emerges from most studies is that the reaction by-products of ozonation appear to be less toxic than those produced by chlorination (for example, chlorohydroxyfuranones, THMs). Two mutagenic by-products, glyoxal acid and glyoxylic acid, were identified after ozonation of naphthoresorcinol, which has some structural analogy with the humic model. On the other hand, it is shown that several carcinogens and pesticides can be destroyed by ozone. Ozonation of polyaromatic amines and polycyclic aromatic hydrocarbons eliminated or reduced the mutagenic activity of these compounds.

2.6. Ozone in the treatment of waters and waste waters.

Ozone application has increased enormously both in number and diversity since the first full scale application of ozone for the disinfection of drinking water in Nice (1906). It is used for the treatment and purification of ground and surface waters, for domestic and industrial waste water as well as in swimming pools and cooling tower systems. It has also been integrated into production processes that utilize its oxidizing potential, e.g. bleaching in the pulp and paper industry, metal oxidation in the semiconductor industry. In Table 2.4 it is shown the number of ozone production plants built by German industrial companies during the last 43 years and fields of application.

Table 2.4. Number of ozone production plants built by German industrial companies from 1954-1997 and fields of application (Böhme, 1999).

Field of Application	Total no. of plants	% of Total	Typical ozone dosage	Unit of ozone dosage
<i>Drinking Water Treatment</i>				
Drinking Water	694	10.5	0.5-1.2	$\text{g O}_3 \cdot \text{m}^{-3}$
Beverage industry	772	12		
<i>Waste Water Treatment</i>				
Process water	660	10	0.5 -> 3.5	$\text{g O}_3 \cdot \text{m}^{-3}$
Waste water or exhaust air	221	3	2 – 50/ 5 - 20	$\text{g O}_3 \cdot \text{m}^{-3}$
Leachate	32	0.5	0.5 – 3.0	$\text{g O}_3 \cdot \text{g}^{-1} \Delta \text{COD}$
Textile industry	6	<0.1	> 0.13	$\text{g O}_3 \cdot \text{g}^{-1} \Delta \text{COD}$
Pulp bleaching	9	<0.1	-	-
Cooling water	47	0.7	-	-
<i>Other applications</i>				
Swimming pool water	3587	55	1.0 (28°C) 1.5 (35°C)	$\text{g O}_3 \cdot \text{m}^{-3}$
Others	536	8		
<i>Total</i>	6566	100		

Generally, the main areas where ozone is used are:

- Disinfection
- Oxidation of inorganic compounds
- Oxidation of organic compounds, including taste, odor, color removal and
- Particle removal.

2.6.1. Drinking water treatment (Mark et al., 1996; Gottschalk et al., 2000)

Drinking water supplies are based on natural ground waters, on artificially recharged ground waters or bank filtered surface waters, on lakes and dam reservoirs and on river waters. Ozone is typically applied as a pre-disinfectant for the control of algae and inactivation of bacteria and viruses in direct filtration processes, and as a pre- and/or intermediate oxidant for inorganic and organic matter to eliminate taste, odor, and color compounds; remove turbidity, metal ions; and reduce levels of trihalomethane (THM) and related organic precursors.

- Disinfection: The introduction of ozone in water treatment started about a century ago and was directed at the disinfection of microbiologically polluted water. Ozone is very effective against bacteria because even concentrations as low as 0.01 ppm are toxic to bacteria (Mark et al., 1996). Ozone is a more effective broad-spectrum disinfectant than chlorine-based compounds. Whereas disinfection of bacteria by chlorine involves the diffusion of HOCl through the cell membrane, disinfection by ozone occurs with the rupture of the cell wall. The disinfection rate depends on the type of organism and is affected by ozone concentration, temperature, pH, turbidity, oxidizable substances, and the type of contactor employed. In the design of chemical disinfection, the concept of $c-t$ (free disinfectant concentration c multiplied by the available contact time t) is frequently applied, based on the law of Chick/Watson (1908). Very often, a $c-t$ value of 1.6 – 2 $\text{mg}\cdot\text{L}^{-1}\cdot\text{min}^{-1}$ (e.g. 0.4 $\text{mg}\cdot\text{L}^{-1}$ ozone for 5 min) is considered to be sufficient for effective disinfection, after particulate matter is removed down to low turbidities.
- Oxidation of Inorganic Compounds. Whereas the use of ozonation to oxidize metal surfaces in the semiconductor industry is growing, ozonation for the oxidative removal or transformation of inorganic constituents of drinking and waste waters is a rather rare application, because other methods exist for most of the target compound. However, inorganic compounds may be oxidized as a secondary effect of ozonation for other purposes (particle removal, organics oxidation). Table 2.5 provides an overview of the target and product compound and the rate of oxidation in drinking and waste waters. A critical reaction is here the formation of bromate, a potential carcinogen, from bromide in the water source, for which the European Union has set a limit value of 10 $\mu\text{g}\cdot\text{L}^{-1}$ (Gottschalk et al., 2000). Possible measures to limit bromate formation are: adjusting the ozone dosage, or dosing a small amount of ammonia or hydrogen peroxide.

Table 2.5. Oxidation of inorganic compounds by ozonation (Langlais et al., 1991; Hoigné et al., 1985)

Compound	Products	Rate of oxidation	Remarks
Fe ²⁺	Fe(OH) ₃	Fast	Filtration of solids required; application in the beverage industry
Mn ²⁺	MnO(OH) ₂	Fast	Filtration of solids required; application in the beverage industry
	MnO ₄ ⁻	Fast	At higher residual ozone conc., reduction and filtration required
NO ₂ ⁻	NO ₃ ⁻	Fast	Nitrite is a toxic compound
NH ₄ ⁺ / NH ₃	NO ₃ ⁻	Slow at pH<9 Moderate at pH>9	Not relevant
CN ⁻	CO ₂ , NO ₃ ⁻	Fast	Application in waste water
H ₂ S / S ²⁻	SO ₄ ²⁻	Fast	Not relevant
As-III	As-V	Fast	Preoxidation for subsequent As- removal
Cl ⁻	HOCl	Near zero	Not relevant
Br ⁻	HOBr / OBr ⁻ , BrO ₃ ⁻	Moderate	Bromination of organic compounds possible; bromate as toxic by-product
I ⁻	HOI / OI ⁻ , IO ₃ ⁻	Fast	Not relevant
HOCl / OCl ⁻	ClO ₃ ⁻	Slow	Loss of free chlorine
Chloroamines, Bromamines		Moderate	Loss of combined chlorine
ClO ₂	ClO ₃ ⁻	Fast	Loss of free chlorine dioxide
ClO ₂ ⁻	ClO ₃ ⁻	Fast	
H ₂ O ₂	OH [·]	Moderate	Basis of O ₃ /H ₂ O ₂ – process (AOP)

- Oxidation of organic compounds. All water sources may contain natural organic matter (NOM), but concentrations (usually measured as dissolved organic carbon, DOC) differ from 0.2 to more than 10 mg.L⁻¹. The tasks of NOM-ozonation are (Camel and Bermond, 1998):
 - Removal of color and UV-absorbance: surface waters generally are colored by naturally occurring organic materials such as humic, fulvic, and tannic acids. Such color-causing compounds contain multiple conjugated double bonds, some of which are readily split by ozone (specific ozone consumptions in the range below 1 g O₃.g⁻¹ DOC).

- Increase in biodegradable organic carbon ahead of biological stages: for optimal production of biodegradable DOC specific O_3 -consumptions of about $1 - 2 \text{ g.g}^{-1}$ are advised.
- Reduction of potential disinfection by-product formation, including trihalomethanes: trace concentrations of organic materials in treated water with chlorine produce THMs. Because some of these compounds are carcinogenic, the EPA (Environmental Protection Agency) has set the maximum contaminant level for total THMs at 0.1 mg/L. The main strategy for controlling THMs is to reduce their precursors. In preozonation, ozone is added in low dosage levels at the front of the plant to aid the coagulation and partial removal of THM precursors. The reduction in DBP-formation also depends on the specific ozone consumption. Typical reductions are in the range of 10 to 60% (compared to no-ozonated water), at specific ozone dosages between 0.5 to $2 \text{ g } O_3.\text{g}^{-1}$ DOC initially present.
- Direct reduction of DOC/TOC-levels by mineralization: less relevant and applicable, because of the high ozone demand for direct chemical mineralization, with typically more than $3 \text{ g } O_3.\text{g}^{-1}$ DOC initially present needed to achieve a removal efficiency of 20% or more.

Organic micropollutants are found in surface and ground waters, always in conjunction with more or less NOM, but at relatively low concentrations in the range of $0.1 \mu\text{g.L}^{-1}$ to $100 \mu\text{g.L}^{-1}$ (in water sources of sufficient quality for a water supply). In practical ozone applications, trace organic oxidation has not been a primary task, but was considered to be a positive side effect. A qualitative presentation of expected degrees of removal in full-scale drinking water treatment plants is presented in Table 2.6.

- Particle removal processes. Turbidity in water is removed by ozonation through a combination of chemical oxidation and charge neutralization. Colloidal particles that cause turbidity are maintained in suspension by negatively charged particles which are neutralized by ozone. Ozone further alters the surface properties of colloidal materials by oxidizing the organic materials that occur on the surface of the colloidal spherical particles. Optimal dosage exists, typically in the range of 0.5 mg.L^{-1} .

Table 2.6. Degree of removal of trace organics during ozonation in full-scale drinking water treatment plants (Gottschalk et al., 2000)

Substances	Degree of removal, range in %	Remarks
Taste and odor	20 - 90	Source specific
Methylisoborneol geosmin	40 –9 5	Improvements by AOPs: O ₃ /H ₂ O ₂ and O ₃ /UV
Alkanes	<10	
Alkenes and chlorinated alkenes	10 - 100	Chlorine content important, AOP support oxidation
Aromatics and chloroaromatics	30 – 100	Highly halogenated phenols are more difficult to oxidize
Aldehydes, alcohols, carbonic acids	Low	Typical products of ozonation , easily biodegradable
N-containing aliphatics and aromatics	0 – 50	AOP may increase oxidation rate
Pesticides	0 – 80	Very specific to substance, triazines require AOP
Polyaromatic hydrocarbons	high, up to 100	

2.6.2. High purity water systems (Mark et al., 1992)

- Bottling and canning plants: breweries ozonate the brewing water to remove any residuals of taste and odor and to ensure the absence of microorganisms. The soft drink industry removes the ozone residual by vacuum-stripping in a degassing chamber before bottling. The bottled water industry requires that an ozone residual be included with the water in the bottle. The ozone residual disinfects the inside of the bottle where contact is made with the water; some ozone, however, escapes into the gas phase where it also disinfects the inside of the cap and the container, which is not in contact with water. Finally, the ozone residual disappears as it decomposes to oxygen. In similar applications, the inside of bottles and cans is sprayed with water containing an ozone residual for disinfection prior to the introductions of food.
- Pharmaceutical industry: sterility of deionized water systems is maintained by using an ozone residual which concentration is maintained at > 0.3 ppm. Prior to product compounding, the ozone residual is removed by contact with UV irradiation for < 1 s.

- Electronics industry: highly purified water is required for water washing between the various process steps. Ozone protects these systems from biological fouling without causing ionic or microparticle contamination.

2.6.3. Ozonation in waste water treatment (Gottschalk et al., 2000)

One of the first industrial ozone waste water applications involved the oxidation of phenol and cyanide, together with the treatment of textile-dye waste water, remain the three largest applications of ozone to industrial wastes. Effluents possessing either natural color bodies, e.g., tannins and lignins from pulp and paper operations, or synthetic color bodies, can be decolorized by ozone.

Full-scale waste water ozone treatment facilities may roughly be defined as systems with a ozone generation capacity of more than 0.5 kg per hour. They can be found in various applications in all branches of industry, treating almost all types of waste waters. In many full-scale applications the variable costs for energy and oxygen are regarded as economically decisive. The most frequently used contactors in full-scale waste water ozonation systems are bubble column reactors equipped with diffusers or venturi injectors.

- Disinfection. Disinfection of waste water before discharge into receiving waters is sometimes required to meet water quality standards in some countries or desired when treated waste water effluent is directly reused for irrigation or process water applications.
- Oxidation of Inorganic compounds. Ozonation of inorganic compounds in waste waters with the aim to destroy toxic substances is mostly restricted to cyanide removal (Böhme, 1999). Cyanide is frequently used in galvanic processes in the metal processing and electronics industry, where it can appear as free cyanide but more often occurs in complexed forms associated with iron or copper. While ozone reacts so fast with free cyanide, complexed cyanides are more stable to the attack of molecular ozone. Nitrite (NO_2^-) as well as sulfide ($\text{H}_2\text{S}/\text{S}^{2-}$) removal from waste waters is sometimes performed by ozonation.
- Oxidation of organic compounds. The majority of problematic substances in industrial waste waters are organic compounds. Often a complex mixture, composed of many individual substances present in a wide range of concentrations (from mg to $\text{g}\cdot\text{L}^{-1}$), has to be treated. The predominant tasks associated with ozone treatment of waste waters are:
 - The transformation of toxic compounds (often occurring in comparatively low concentrations in a complex matrix)

- The partial oxidation of the biologically refractory part of the DOC, mostly applied with the aim to improve subsequent biodegradation
- The removal of color

Full-scale ozonation systems have been used to treat waste waters, such as landfill leachates, as well as waste waters from the textile, pharmaceutical and chemical industries. The main pollutants associated with these waters are refractory organics, which can be characterized as:

- Humic compounds (brown or yellow colored) and adsorbable organic halogens (AOX) in the landfill leachates,
 - Colored (poly-)aromatic compounds often incorporating considerable amounts of metal ions (Cu, Ni, Zn, Cr) in textile waste waters,
 - Toxic or biocidal substances (e.g. pesticides) in the pharmaceutical and chemical industry,
 - Surfactants from the cosmetic and other industries,
 - COD and colored compounds in solutions of the pulp and paper production.
- Particle removal processes. The ozonation of municipal waste water can also be used to enhance particle removal, although this must be regarded as a side-effect.

2.6.4. Advantages and disadvantages of using ozone

Ozone presents some advantages for its use in water treatment, specially over chlorine, but there are also several disadvantages (Prado et al., 1992).

Advantages

- Ozone is easy to produce from air or oxygen by electric discharge.
- Ozone reacts readily with organic and inorganic compounds due to its high reduction potential and reactivity.
- Generally, it does not produce more toxic compounds than removed ones, and neither introduces foreign matter to the medium, fact that chlorine does.

- Along with disinfection, ozone also lowers the COD, color, odor and turbidity of the water treated.
- Possible excesses of ozone in water decompose readily to oxygen, without leaving any residue.

Disadvantages

- The yield of ozone generator is low (6-12% from oxygen and 4-6% from air), and ozone concentration is low as well.
- Ozone has to be generated on-site because its problems to be stored and transported.
- Generally, controlling step of the oxidation with ozone is the mass transfer of ozone into water. Then, it is interesting ozone generators producing high ozone concentrations.
- As ozone half-life in the distribution system is about 25 minutes at ambient temperature, ozonation does not assure purity of drinking water and some chlorine has to be added.

