

Bottom line: Cold water with pH around or below 7.2 holds Ozone in the water for a longer time.

<http://www.lenntech.com/library/ozone/decomposition/ozone-decomposition.htm>

Ozone decomposition

When [ozone](#) is produced it will decay rapidly, because ozone is an instable compound with a relatively short half-life. The half-life of ozone in water is a lot shorter than in air (see table 1). Ozone decays in water under drinking water conditions (pH: 6-8,5), partly in reactive OH-radicals. Therefore, the assessment of an ozone process always involves the reactions of two species: ozone and OH-radicals. When these OH-radicals are in the dominant particles in the solution, it is called an advanced oxidation process (AOP). The decay of ozone in OH-radicals in natural waters is characterized by a fast initial decrease of ozone, followed by a second phase in which ozone decreases by first order kinetics [15]. Dependent on the quality of the water, the half-life of ozone is in the range of seconds to hours. Factors influencing the decomposition of ozone in water are temperature, pH, environment and concentrations of dissolved matter and UV light. Here, the main influence factors for ozone decomposition will be discussed.

Influence factors

1. Temperature

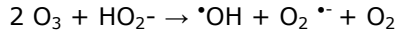
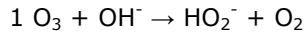
Temperature has an important influence on the half-life of ozone. Table 1 shows the half-life of ozone in air and water. In water the half-life of ozone is much shorter than in air, in other words ozone decomposes faster in water [1]. The solubility of ozone decreases at higher temperatures and is less stable. On the other hand, the reaction speed increases with a factor 2 or 3 per 10 °C [5,6]. Principally, ozone dissolved in water cannot be applied when temperatures are above 40 °C, because at this temperature the half-life of ozone is very short.

Table 1: half-life of ozone in gas and water at different temperatures

Air		Dissolved in water (pH 7)	
Temp (°C)	Half live	Temp (°C)	Half live
-50	3 months	15	30 min
-35	18 days	20	20 min
-25	8 days	25	15 min
20	3 days	30	12 min
120	1,5 hours	35	8 min
250	1,5 seconds		

2. pH

As mentioned above, ozone decomposes partly in OH-radicals. When the pH value increases, the formation of OH-radicals increases. In a solution with a high pH value, there are more hydroxide ions present, see formulas below. These hydroxide ions act as an initiator for the decay of ozone:



The radicals that are produced during reaction 2 can introduce other reactions with ozone, causing more OH-radicals to be formed.

In addition the pH influences acid/base equilibriums of some compounds and also the reaction speed of [ozone](#). This applies also to the reaction with scavenger CO_3^{2-} , which is also pH dependant (Pka $\text{HCO}_3^{2-}/\text{CO}_3^{2-} = 10,3$).

Figure 1 shows that the decay of ozone in a basic environment is much faster than in an acid environment.

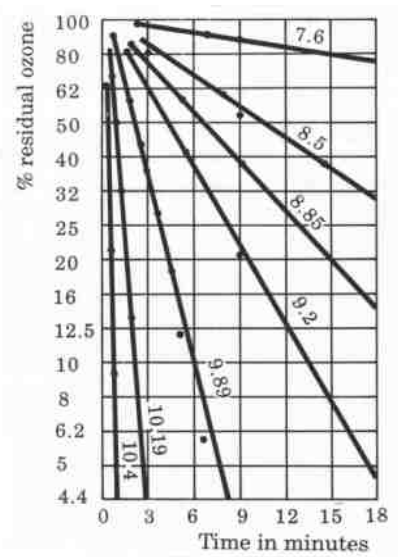


Figure 1: effect of the pH on the decay of ozone ($T = 15 \text{ }^\circ\text{C}$)

3. Dissolved solids concentration

Dissolved ozone can react with a variety of matter, such as organic compounds, viruses, bacteria, etc. As a result, ozone decomposes to other matter; see figure 2. This figure illustrates that the half-life of ozone in distilled water is much shorter, compared to tap-water.

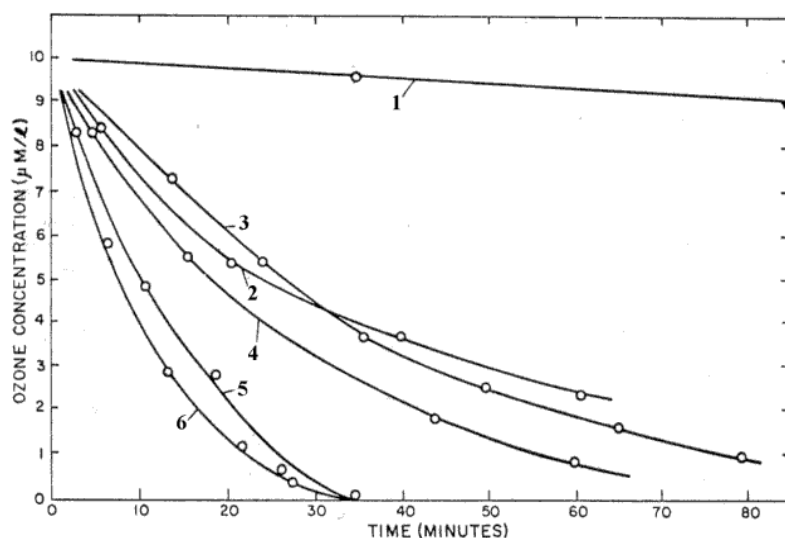


Figure 2: Ozone decomposition in different types of water at 20 °C. 1 = double-distilled water; 2 = distilled water; 3 = tap water; 4 = groundwater of low hardness; 5 = filtered water from Lake Zurich (Switzerland); 6 = filtered water from the Bodensee (Switzerland)

Ozone decomposes in water in OH-radicals. Dependent on the nature of the dissolved matter, these can accelerate (chain-reaction) or slow down the decay of ozone. Substances that accelerate this reaction are called promoters. Inhibitors are substances that slow down the reaction.

When water is ozonized, one often uses the term 'scavenging capacity'. Scavengers are entities that react with OH-radicals and slow down the chain-reaction. The scavenging capacity can be defined as follows [16]:

$$k_{\text{OH-DOC}}[\text{DOC}] + k_{\text{OH-HCO}_3^-}[\text{HCO}_3^-] + k_{\text{OH-CO}_3^{2-}}[\text{CO}_3^{2-}]$$

4. Carbonate and bicarbonate

Scavengers slow down the chain-reaction. This is because after the reaction of scavengers with OH-radicals, the reaction products do not react with ozone any further. Carbonate is a scavenger with a strong effect. The addition of carbonate (CO_3^{2-}) can increase the half-life of ozone [5,6]. The effect on the reaction speed is highest at low concentrations. Above 2 mmol l⁻¹ for ozonisation and 3 mmol l⁻¹ for advanced oxidation process (AOP), the decrease in the reaction speed is negligible [6].

When a solution mainly undergoes indirect reactions (with OH-radicals), for instance in a solution with a high pH value or an AOP-process, the presence of scavengers is undesired. The scavengers react very fast with OH-radicals and lower the oxidation capacity. For this kind of processes a low scavenging capacity is required.

Carbonate (CO_3^{2-}) ions are a much stronger scavengers than bicarbonate (HCO_3^{2-}) ions (reaction speed CO_3^{2-} : $k = 4,2 * 10^8 \text{ M}^{-1}\text{s}^{-1}$ and reaction speed HCO_3^- : $k = 1.5 * 10^7 \text{ M}^{-1}\text{s}^{-1}$). That is why in an ozone process under drinking water conditions, the bicarbonate concentration is less important [6]. Figure 3 illustrates the relation of the carbonate ratio, bicarbonate ratio and pH.

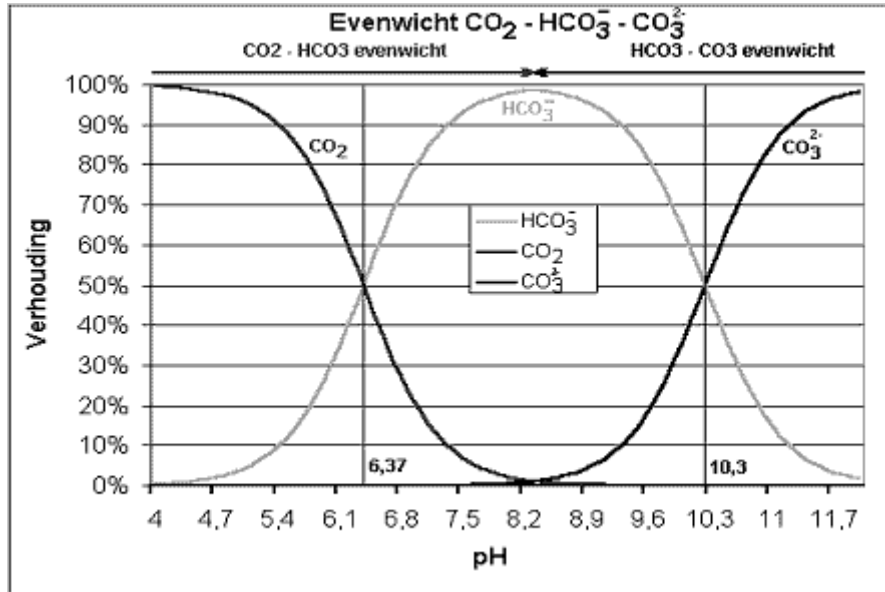


Figure 3: equilibrium carbonate, bicarbonate and [carbon dioxide](#)

5. Natural Organic Material

Natural organic material (NOM) exists in every kind of natural water and is often measured as dissolved organic carbon (DOC). NOM reduces the quality of the water with regard to color and odor. Ozone can be used in [water treatment](#), for the reduction of the concentration of NOM. The concentration of NOM in natural waters can vary from 0,2 – 10 mg l⁻¹ [6]. The influence of NOM on ozone is twofold. Dependent on the type of NOM, it can be oxidized directly by NOM. This is the case for compounds which easily react with ozone, such as double bonds, activated aromatic compounds, deprotonated amines and sulphide [15]. On the other hand, OH-radicals can react with NOM (indirect reaction) and act as a promoter or as a scavenger.

In natural waters, it is difficult to determine the stability of ozone as a result of the indefinite effect of NOM. That means it is not possible to estimate the fraction that accelerates or slows down the reaction [15].

Read more: <http://www.lenntech.com/library/ozone/decomposition/ozone-decomposition.htm#ixzz0qZ3XxhRE>

Ozone generation

[Henry coefficient](#) [Bunsen coefficient](#) [Solubility ratio coefficient](#) [Influencing the solubility](#)

[Mass transfer](#) [Ozone injection techniques](#)

To disinfect (waste)water with ozone, ozone must be dissolved in water. Ozone gas is produced on-site by an [ozone generator](#). It can be dissolved in water in various ways.

To bring about a proper disinfection and oxidation, the ozone concentration must be as high as possible. The prediction of [ozone](#) solubility is more complicated than for other gasses, because ozone solubility is influenced by several factors, such as temperature, pH and dissolved matter. This is a consequence of the instability of ozone in water. The solubility of a gas in water is usually defined by Henry's law. For the solubility of ozone the Bunsen (β) and particularly the solubility ratio (S) factor is used.

Henry coefficient

Henry's law states that the solubility of a gas in a liquid is proportional to the pressure of the gas over the liquid. Principally, Henry's law can only be applied on gasses that do not chemically change in water, during transfer.

$$Y = HX$$

Y = pressure of substance over fluid [atm]

X = molar fraction ozone (gaseous) [-]

H = Henry [atm/l/mol]

An ozone generator produces ozone in a mixed form, so the term partial pressure is used. The partial pressure of a gas in a mixture (here: ozone) is its contribute to the total pressure of the mixture. Figure 1 describes the solubility of ozone at different pressures. In practice this will be less, because above a certain feed gas concentration stabilisation will occur [10]. Nowadays, much higher ozone concentrations are used to dissolve ozone in water. Lenntech delivers [generators](#) that produce ozone concentrations of 240 g/Nm³.

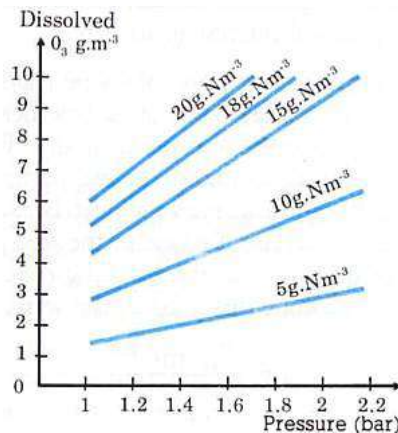


Figure 1: effect of pressure and feed gas concentration on ozone solubility

Henry coefficient (Hc)

Y = Concentration of gas above the liquid in equilibrium with the gas dissolved in the liquid, mg/l

X = Concentration of gas in the liquid in equilibrium with the gas above the liquid, mg/l

Hc = (mg gas/liter of gas)/ (mg gas/liter of liquid)

This form of Henry is more practical because the terms are expressed in mg/l.

Bunsen coefficient (β)

The solubility of [ozone](#) can also be calculated with the Bunsen adsorption coefficient [5]. The formula that can be used to calculate the solubility is:

$$C_s = \beta * M * P$$

C_s = Concentration dissolved gas (kg/m^3)
 B = Bunsen adsorption coefficient (-)
 M = Density of the gas (kg/m^3)
 P = Partial pressure (Pa)

The Bunsen adsorption coefficient is expressed as a volume of gas at NTP (normal pressure and temperature), which is dissolved at equilibrium by a unit volume of liquid at a given temperature, when the partial pressure of the gas is the unit atmosphere. The Bunsen coefficient has no dimension.

$$\beta = V_g / V_l$$

Solubility ratio coefficient

In general the mentioned formulas are not very practical, although they are used alternately (with the exception of the derived Hc coefficient). Another more practical method to calculate the solubility is by using the solubility ratio coefficient. This solubility ratio is given as mg/l per liter in water to mg/l in gas. This factor is dimensionless and relates to the Henry coefficient [6]. The relation between these constants is defined as follows:

$$H = \frac{pO_3}{S \times C_g}$$

$$S = \frac{1}{H_c}$$

H = Henry (atm/l/mol)
 pO_3 = partial pressure ozone (Pa)
 C_g = concentration ozone gas (kg/m^3)
 S = solubility factor (-)
 H_c = Henry's constant (-)

Figure 2 illustrates the solubility ratio (S) at increasing temperature, carried out by different researchers. The solubility is studied at different ion concentrations (μ). This figure illustrates that the solubility of ozone is influenced by several factors in the water.

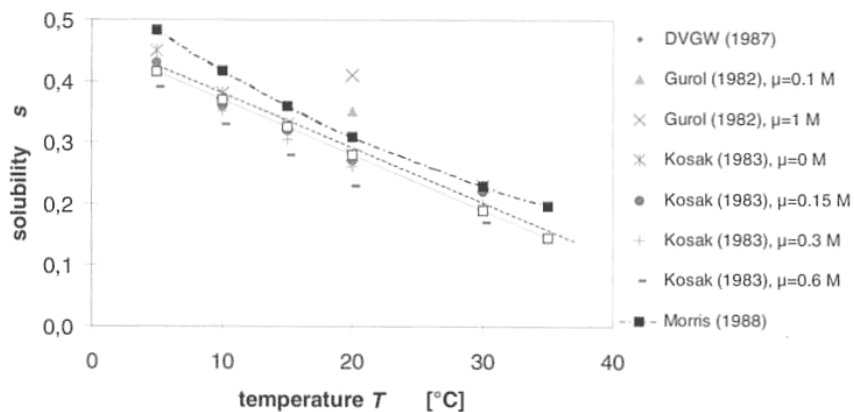


Figure 2: ozone solubility (S) as a function of the temperature (T = 5-35 °C)

The following formula can be used to calculate of the solubility ratio (S) at different temperatures:

$$\log_{10}s = -0,25 - 0,013T \text{ [}^\circ\text{C]}$$

This formula is more of a guideline because the real ozone concentration is influenced by a number of factors in the water. On the other hand, that the temperature is one of the most important factors influencing the solubility.

An computation of this coefficient at 20 °C:

$$\begin{aligned}\log_{10}s &= -0,25 - 0,013T \\ \log_{10}s &= -0,25 - 0,013 * 20 \\ \log_{10}s &= -0,51 \\ s &= 10^{-0,51} \\ s &= 0,31\end{aligned}$$

At 20 °C the solubility ratio coefficient $s = 0,31$ mg/l water per mg/l carrying gas (see also figure 2). For example at 20 mg/l ozone in air, $20 * 0,31 = 6,2$ mg/l will dissolve in water at 20°C.

Influencing the solubility

The degree of solubility of ozone gas is dependant on the concentration in gas and thus dependant on the partial pressure. Another important factor influencing the solubility is the temperature. Besides temperature, pH and ion concentration in the solution are the main factors influencing the solubility. Summarized, the solubility can be increased by:

- Increasing the ozone concentration in the air (oxygen);
- Increasing air pressure (oxygen);
- Decreasing the water temperature;
- Decreasing the amount of solutes;
- Decreasing the pH;
- Excess of UV-light.

Mass-transfer

When matter is transferred from one phase to another across a gas-liquid interface, a concentration gradient will occur in each phase because of a resistance. This transfer into another phase is called mass-transfer and is represented by figure 3 (double-layer model). During the transfer of ozone from gas to liquid, the following stages are processed: diffusion of ozone across the gas/liquid phase, dissolving into the liquid, diffusion into the liquid.

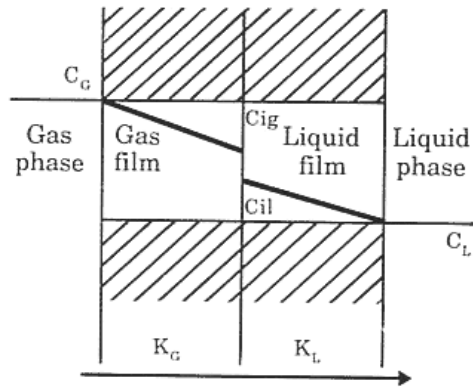


Figure 3: model for ozone transfer

The transfer rate is dependant on [10]:

- The physical properties of gas and liquid
- The difference in concentration across the surface
- Turbulence

Ozone injection techniques

Ozone can be injected in water in several ways. The most commonly used techniques are [diffuser and venturi](#) [33,52]. A diffuser often exists of a disc or bar. A diffuser works under pressure and creates a bubble column. Advantages of a diffuser system are high yield, simple construction and advantageous for high water volumes (i.e. drinking water systems). Disadvantages are that it is not a very compact system and the efficiency depends on contact column dept and bubble size. Moreover, a diffuser can be stuffed-up, causing the efficiency to decrease. Here, you can see an application of a diffuser system (counter- and equal-flow contact column):

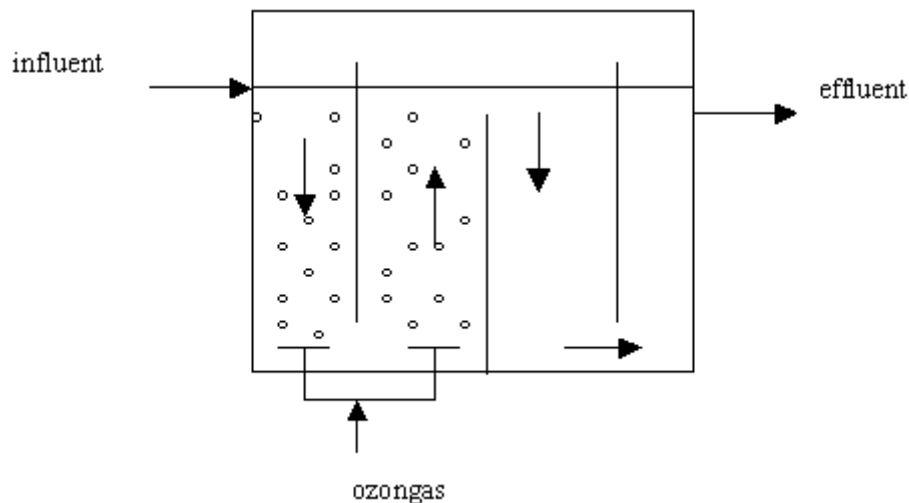


Figure 4: counter- and equal-flow contact column

In case of a venturi system, the ozone gas is dissolved in water by pressure. Pressure creates a constriction in the fluid flow, causing suction of ozone (figure 5). A venturi system has

various benefits, namely: compact installation, no moving particles, high yield.



Figure 5: venturi system

Read more: <http://www.lenntech.com/library/ozone/transfer/ozone-transfer-mechanisms.htm#ixzz0qZ7f9juh>