

Chemistry of Dissolved Oxygen in Aquaculture

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[DOI:10.5281/FishWorld.15822867](https://doi.org/10.5281/FishWorld.15822867)

Abstract

Aquaculture is a rapidly growing sector that provides an affordable and essential source of dietary protein. To meet the increasing demand driven by population growth, culture practices are becoming more intensive. One of the key aspects of successful aquaculture management is maintaining optimal dissolved oxygen (DO) levels in the culture systems. However, the underlying chemistry of DO dynamics in aquatic environments is often not clearly understood. DO levels in aquaculture ponds are governed by a complex interplay of multiple factors, including oxygen solubility, biological consumption, and replenishment through photosynthetic primary production. Among these, temperature has a strong negative correlation with oxygen solubility, while partial pressure exhibits a positive relationship. Salinity, pH, and the presence of other gases and dissolved salts also influence oxygen availability, often reducing its solubility. This article explains the physicochemical principles that control dissolved oxygen in aquaculture systems, highlighting the effects of temperature, pH, salinity, gas interactions, and pressure. A clearer understanding of these factors is crucial for effective DO management and sustainable aquaculture practices.

Key words: Dissolved Oxygen, Aquaculture, Temperature, Solubility and Henry's Law

1. Introduction

Earth's atmosphere is composed of a mixture of gases produced through various geological, biological, and atmospheric processes. These gases play a vital role in sustaining ecological balance and environmental functioning. Major atmospheric gases include nitrogen (N₂), oxygen (O₂), carbon dioxide (CO₂), and inert gases such as neon, helium, methane, krypton, and hydrogen. Each gas serves an irreplaceable function, with oxygen being particularly essential for the survival of most living organisms. It makes up about 21% of the

atmosphere and is used in oxidative respiration. Oxygen is released into the atmosphere primarily through photosynthesis, a process carried out by plants and cyanobacteria. A key evolutionary milestone related to atmospheric oxygen is the Great Oxygenation Event (GOE), during which photosynthetic cyanobacteria began producing oxygen in large amounts, permanently altering Earth's atmospheric composition. While terrestrial organisms absorb oxygen in its gaseous form, aquatic organisms such as fish depend on dissolved oxygen (DO), which is absorbed through their gills. DO enters aquatic systems mainly through surface diffusion from the atmosphere and through photosynthetic activity in the water. The efficiency of oxygen diffusion is influenced by temperature, pH, surface area, and to a lesser extent, atmospheric pressure. Cooler temperatures, higher pH, and greater surface contact enhance oxygen solubility. In aquaculture systems, where fish production is increasingly intensified, the availability and fluctuation of DO are critical for health and productivity. Farmers often notice low DO levels after heavy feeding or during early morning hours and rely on aerators without fully understanding the underlying chemical and physical processes. While surface aeration and primary production are recognized contributors, the roles of temperature, pH, and pressure are often underestimated. A clearer understanding of these physicochemical dynamics is essential for better oxygen management and sustainable aquaculture practices.

2. Solubility of gases

The solubility of gases in water refers to how much of a gas can dissolve in water under given environmental conditions. This is a crucial concept in aquatic chemistry, especially in understanding dissolved oxygen (DO) and the availability of other gases like CO₂ and ammonia in aquatic environments, including aquaculture systems. The dissolution of oxygen (O₂) in water is a physical equilibrium process wherein gaseous oxygen transitions into the aqueous phase without undergoing a chemical transformation. This process is governed by Henry's Law, which states that the solubility of a gas is directly proportional to its partial pressure above the liquid. The thermodynamic behavior of this equilibrium is endothermic in nature, meaning the dissolution of oxygen absorbs heat. As a result, an increase in temperature leads to an increase in Henry's law constant (K_h), thereby reducing the solubility of oxygen in water. This temperature dependence is further explained by the van 't Hoff equation, which relates changes in solubility to enthalpy of dissolution. At the molecular level, lower temperatures enhance the retention of dissolved oxygen due to reduced kinetic energy and stronger stabilization by water molecules. In contrast, at higher temperatures, increased molecular motion reduces the ability of water to retain gas molecules, causing more oxygen to escape to the atmosphere.

Consequently, oxygen solubility in natural and aquaculture waters is inversely related to temperature, which has critical implications for aquatic life, particularly under thermal stress and during early morning hours when dissolved oxygen levels are typically at their lowest.

2.1 Detailed description is given below with keeping oxygen as example

To understand this, we need to know what is Henry's law and van 't Hoff equation.

Henry's Law states that the amount of gas dissolved in a liquid is directly proportional to the partial pressure of that gas above the liquid, at a constant temperature. Hence higher the partial pressure of a gas over a liquid, the more of that gas will dissolve in the water

Henry's Law can be expressed as

$$C = K_H P \text{ or } P = C / k_h = K_H \times C, \text{ where } K_H = 1 / k_h.$$

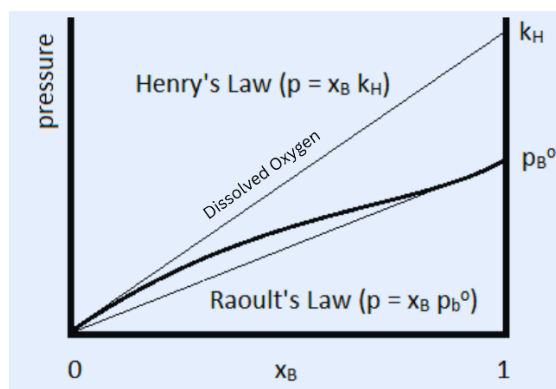
Where:

C = concentration of the dissolved gas in the liquid (mol/L or mg/L)

K_H = Henry's Law constant (depends on the gas and temperature)

P = partial pressure of the gas above the liquid (in atmospheres, atm)

k_h is used in $C = k_h \times P$ to calculate gas concentration from pressure (units: mol/L·atm), while K_H is used in $P = K_H \times C$ to calculate pressure from concentration (units: atm·L/mol); they are reciprocals of each other.



Henry's Law and Raoult's Law both describe how gases and liquids behave, but they apply in different contexts. Henry's Law explains how the amount of gas that dissolves in a liquid is directly proportional to its partial pressure above the liquid, important for understanding how gases like oxygen dissolve in water, such as in aquaculture ponds. In contrast, Raoult's Law applies to liquid mixtures, stating that each component's contribution to total vapor pressure depends on its mole fraction and pure vapor pressure. A simple environmental example of Raoult's Law is the evaporation of oil spills, where lighter components like benzene evaporate faster based on their concentration and volatility.

For instance, consider an aquaculture pond operating under the following conditions:

Air contains 21% oxygen, so the partial pressure of oxygen (PO_2) is: $PO_2 = 0.21 \text{ atm}$

At 25°C, the Henry's Law constant for O₂ in water is approximately: $k_h = 1.3 \times 10^{-3}$ mol/(L·atm)

Using Henry's Law: $C = k_h \times P$

$$C = 1.3 \times 10^{-3} \times 0.21 = 2.73 \times 10^{-4} \text{ mol/L}$$

Convert to mg/L (molar mass of O₂ = 32 g/mol):

$$2.73 \times 10^{-4} \text{ mol/L} \times 32 \text{ g/mol} = 8.74 \text{ mg/L}$$

Therefore, at 25°C, water can saturate a maximum of 8.7 mg/L of oxygen.

But how at 25°C, the Henry's Law constant for O₂ in water is approximately: $k_h = 1.3 \times 10^{-3}$ mol/(L·atm) were assumed? At 25°C, the Henry's Law constant for oxygen (O₂) in water is experimentally determined to be approximately 1.3×10^{-3} mol/(L·atm), based on measured solubility data under equilibrium conditions. Further the relation between temperature and solubility can be explained by van 't Hoff equation. To be more precise, as temperature decreases, the Henry's law constant (K_h) also decreases, leading to an increase in gas solubility can be quantitatively explained by the van 't Hoff equation.

$$\ln(k_h(T) / k_h(T_0)) = (\Delta H_{\text{sol}}^\circ / R) \times (1/T_0 - 1/T)$$

Where:

$k_h(T)$: Henry's constant at temperature T

$k_h(T_0)$: Henry's constant at reference temperature T_0

$\Delta H_{\text{sol}}^\circ$: Enthalpy change of dissolution (usually positive for gases like O₂)

R: Universal gas constant (8.314 J/mol·K)

T, T_0 : Absolute temperatures in Kelvin (K)

This equation quantifies how gas solubility changes with temperature. For most gases, $\Delta H_{\text{sol}}^\circ > 0$, indicating endothermic dissolution. As temperature increases, Henry's constant k_h increases, and gas solubility decreases.

Example: Oxygen (O₂)

At 25°C (298 K): $k_h(T_0) \approx 1.3 \times 10^{-3}$ mol/L·atm

At 10°C (283 K): $k_h(T) < 1.3 \times 10^{-3}$ mol/L·atm (from experimental data)

Assume $\Delta H_{\text{sol}}^\circ \approx +12,000$ J/mol (approximate for O₂)

Now apply the van 't Hoff equation:

$$\ln(k_h(283) / 1.3 \times 10^{-3}) = (12,000 / 8.314) \times (1/298 - 1/283)$$

Solving this gives:

$$\ln(k_h(283) / 1.3 \times 10^{-3}) \approx -0.24$$

$$k_h(283) / 1.3 \times 10^{-3} \approx e^{(-0.24)} \approx 0.79$$

$$k_h(283) \approx 0.79 \times 1.3 \times 10^{-3} \approx 1.03 \times 10^{-3} \text{ mol/L} \cdot \text{atm}$$

At lower temperature (10°C), k_h decreases $\rightarrow$ oxygen solubility increases.

Thus, van't Hoff equation shows that gas solubility decreases with increasing temperature. It helps predict solubility at various temperatures when only one k_h value is known. Oxygen, being non-reactive and sparingly soluble, is a good example of where both Henry's Law and the van 't Hoff equation apply accurately. It is interesting to note that when you know the prevailing temperature in a day one can approximately ascertain the DO in the water under ambient pressure ($\approx 1 \text{ atm}$).

In aquatic systems, gases like ammonia (NH_3) and hydrogen sulfide (H_2S) differ from oxygen and carbon dioxide because they not only dissolve in water but also chemically react with it, forming ionic species such as ammonium (NH_4^+) and bisulfide (HS^-). Their solubility and toxicity are therefore influenced by both temperature and pH. As temperature increases, the equilibrium shifts toward the un-ionized, gaseous forms (NH_3 and H_2S), which are more volatile and toxic to aquatic life. At higher pH, this effect is further amplified, especially in the case of ammonia, where the proportion of toxic NH_3 increases significantly. Thus, unlike inert gases that follow Henry's Law more directly, the solubility and behavior of NH_3 and H_2S in water are governed by both physical and chemical equilibria, making their management in aquaculture and aquatic ecosystems particularly complex and critical.

3. Impact of dissolved salts on solubility of oxygen

In saline water, gas solubility decreases due to a phenomenon known as the "salting-out effect." When salts like NaCl dissolve, they dissociate into ions (e.g., Na^+ , Cl^-) that become surrounded by water molecules, forming hydration shells. This reduces the number of free water molecules available to interact with and dissolve gas molecules such as oxygen (O_2) and carbon dioxide (CO_2), which are nonpolar or weakly polar and rely on weak physical interactions for solubility. As a result, higher salinity interferes with the ability of water to retain dissolved gases, leading to reduced gas solubility. This effect is particularly important in marine aquaculture, where oxygen solubility can be approximately 20% lower than in freshwater under similar temperature and pressure conditions. The impact of the dissolved ions in the solubility of oxygen can be explained by Sechenov (or Setschenow) equation.

$$\text{Log (Cs/Co)} = k_s \cdot [\text{Salt}]$$

Where:

Co: solubility of the gas in pure water

Cs: solubility of the gas in saline water

k_s : Sechenov constant (specific to the gas and salt type)

[Salt]: molar concentration of salt (ionic strength)

3.1 Effect of Salinity on Oxygen Solubility (Using Sechenov Equation)

Let's assume:

$C_o = 8.6$ mg/L in freshwater at 25°C (oxygen solubility)

Salinity = 35 g/L (typical seawater)

$k_s \approx 0.1$ for O_2 in NaCl solution

Using the Sechenov Equation: $\log (C_o / C_s) = k_s \times [\text{Salt}]$

Assuming effective salt concentration $[\text{Salt}] \approx 0.6$ mol/L (approximate ionic strength for 35 g/L seawater):

$$\log (8.6 / C_s) = 0.1 \times 0.6$$

$$8.6 / C_s \approx 10^{0.06} \approx 1.15$$

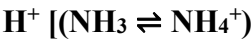
$$C_s \approx 8.6 / 1.15 \approx 7.5 \text{ mg/L}$$

This matches experimental data, where oxygen solubility in seawater is about 7.5 mg/L at 25°C, lower than in freshwater due to the salting-out effect.

4. pH-Dependent Behavior of Dissolved Gases in Water

pH does not directly alter the solubility of oxygen (O_2) in water because oxygen is a non-reactive gas and does not participate in acid-base reactions; instead, its solubility is influenced indirectly by pH through biological and chemical processes. In acidic conditions (low pH), photosynthetic activity may be reduced, leading to lower oxygen production, while microbial and enzymatic processes that consume oxygen may also be suppressed. In alkaline conditions (high pH), photosynthesis can be enhanced, raising daytime oxygen levels, but may lead to sharp nighttime drops due to increased respiration. Additionally, extreme pH levels can alter redox conditions, promoting chemical reactions (e.g., metal or sulfide reduction) that consume dissolved oxygen. In contrast, ammonia (NH_3) is a reactive gas that exists in equilibrium with its ionized form ammonium (NH_4^+), and this equilibrium is strongly influenced by both pH and temperature. At higher pH and temperature, the equilibrium shifts toward the un-ionized NH_3 form, which is more toxic to aquatic life. Therefore, while oxygen's solubility decreases gradually with rising temperature and is only indirectly affected by pH, ammonia becomes increasingly toxic under the same conditions due to changes in chemical speciation. This distinction is crucial in aquaculture, where managing pH and temperature is essential to minimize toxic ammonia exposure while maintaining adequate oxygen levels for fish health.

Mathematical Relationship (Acid Dissociation Constant):



$K_b (NH_3) = \{[NH_4^+] [OH^-]\} / [NH_3]$ or $pK_a (NH_4^+) \approx 9.25$

The fraction of un-ionized ammonia as a function of temperature and pH is presented in the following table.

pH	Temp.	6	8	10	12	14	16	18	20	22	24	26	28	30
7		0.0013	0.0016	0.0018	0.0022	0.0025	0.0029	0.0034	0.0039	0.0046	0.0052	0.006	0.0069	0.008
7.2		0.0021	0.0025	0.0029	0.0034	0.004	0.0046	0.0054	0.0062	0.0072	0.0083	0.0096	0.011	0.0126
7.4		0.0034	0.004	0.0046	0.0054	0.0063	0.0073	0.0085	0.0098	0.0114	0.0131	0.015	0.0173	0.0198
7.6		0.0053	0.0063	0.0073	0.0086	0.01	0.0116	0.0134	0.0155	0.0179	0.0206	0.0236	0.0271	0.031
7.8		0.0084	0.0099	0.0116	0.0135	0.0157	0.0182	0.0211	0.0244	0.0281	0.0322	0.037	0.0423	0.0482
8		0.0133	0.0156	0.0182	0.0212	0.0247	0.0286	0.033	0.0381	0.0438	0.0502	0.0574	0.0654	0.0743
8.2		0.021	0.0245	0.0286	0.0332	0.0385	0.0445	0.0514	0.059	0.0676	0.0772	0.088	0.0998	0.1129
8.4		0.0328	0.0383	0.0445	0.0517	0.0597	0.0688	0.079	0.0904	0.1031	0.1171	0.1326	0.1495	0.1678
8.6		0.051	0.0593	0.0688	0.0795	0.0914	0.1048	0.1197	0.1361	0.1541	0.1737	0.195	0.2178	0.2422
8.8		0.0785	0.0909	0.1048	0.1204	0.1376	0.1566	0.1773	0.1998	0.2241	0.25	0.2774	0.3062	0.3362
9		0.119	0.1368	0.1565	0.1782	0.2018	0.2273	0.2546	0.2836	0.314	0.3456	0.3783	0.4116	0.4453
9.2		0.1763	0.2008	0.2273	0.2558	0.2861	0.318	0.3512	0.3855	0.4204	0.4557	0.4909	0.5258	0.5599
9.4		0.2533	0.2847	0.318	0.3526	0.3884	0.4249	0.4618	0.4985	0.5348	0.5702	0.6045	0.6373	0.6685
9.6		0.3496	0.3868	0.4249	0.4633	0.5016	0.5394	0.4762	0.6117	0.6456	0.6777	0.7078	0.7358	0.7617
9.8		0.46	0.5	0.5394	0.5778	0.6147	0.6499	0.6831	0.714	0.7428	0.7692	0.7933	0.8154	0.8351
10		0.5745	0.6131	0.6498	0.6844	0.7166	0.7463	0.7735	0.7983	0.8207	0.8408	0.8588	0.8749	0.8892
10.2		0.6815	0.7152	0.7463	0.7746	0.8003	0.8234	0.8441	0.8625	0.8788	0.8933	0.906	0.9173	0.9271

5. Conclusion

The chemistry of dissolved oxygen in aquatic systems is fundamental to successful aquaculture operations, governing the survival, growth, and health of cultured species. This complex system is influenced by multiple interconnected factors including temperature, salinity, organic loading, photosynthesis, and microbial respiration, all of which must be carefully managed in intensive aquaculture settings. The growing intensification of aquaculture operations has increased both oxygen demand and the complexity of maintaining optimal dissolved oxygen levels. Climate change further threatens these delicate systems through rising temperatures that reduce oxygen solubility and disrupt natural oxygen dynamics. Understanding the intricate chemistry of dissolved oxygen is therefore crucial for developing effective management strategies and monitoring protocols.

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