

Oxygen in Lakes

A. Solubility

Oxygen is sparingly soluble in water. At equilibrium with the atmosphere, the maximum concentration of O₂ in water (at sea level, 760 mm Hg and at 0 degrees C) is just 14.16 parts per million (0.0014%). In contrast, the concentration of O₂ in the atmosphere is nearly 21%. It is therefore not surprising that oxygen is often a serious constraint on the distribution of aerobic organisms in water. Hutchinson (1957): "A skillful limnologist can probably learn more about the nature of a lake from a series of oxygen determinations than from any other kind of chemical data." p575

1. Henry's law: The mass of a slightly soluble gas that dissolves in a definite mass of a liquid at a given temperature is very nearly directly proportional to the partial pressure of that gas. This holds for gases that do not unite chemically with the solvent.

2. The equilibrium solubility of oxygen in water is strongly influenced by temperature. (See table 15-1, p227, Kalf))

Oxygen concentration, atmospheric pressure 760 mm Hg.

Temperature	Oxygen concentration at saturation
0 C	14.16
5	12.37
10	10.92
15	9.76
20	8.84
25	8.11
30	7.53
35	7.04

Comment: It is apparent that as water temperature increases, the solubility of oxygen decreases. At the same time, most biochemical processes, including those that lead to the consumption of oxygen, are speeded up at higher temperatures. It is not surprising that elevated temperatures sometimes provoke oxygen stress in aquatic organisms.

3. Effect of altitude.

An increase in altitude leads to a lower atmospheric pressure, including a lower partial pressure of oxygen. (See table 15-2, p227, Kalff) The values in the table (above) can be corrected for atmospheric pressure by multiplying by:

$$(P_h - p_w)/(760-p_w)$$

where: P_h = total atmospheric pressure at the location in question, and
 p_w = partial pressure of water vapor at the observed temperature.

Lakes at very great altitude will correspondingly have lower concentration of oxygen.

4. Kinetic considerations.

The rate of movement of a gas across an interface is given by Bohr's equation:

$$dO_2/dt = a \alpha (P - p_t)$$

where: a = area (can be unity)
 α = entrance coefficient
 P = observed partial pressure of the gas
 p_t = the pressure at which the concentration of gas at time t in the water would be in equilibrium.

Experimental analysis indicates a value of α of about 3.5×10^5 mg/m²/day/atmosphere for oxygen. For the surface of a lake, this means that no oxygen gradient is likely to develop in the surface layer provided the layer is well mixed (usually the case). However, a very deep lake may re-stratify before the invasion of atmospheric oxygen during the spring overturn has re-saturated a depleted water column. Hutchinson constructed a table (incorporating various assumptions of the physical mechanisms involved) which provides estimates of the time required for a lake initially at 80% saturation throughout the water column during spring circulation to attain a particular degree of saturation by invasion of atmospheric oxygen.

Oxygenation of ideal lakes at vernal circulation [after Table 75, Hutchinson, p593].

Percentage saturation at time t	80%	90 %	95 %	99 %	99.9 %
Time t for a lake 12.5 m deep	0 days (start)	1.55 days	3.12 days	6.78 days	11.98 days
Time t for a lake 100 m deep	0 days (start)	12.4 days	25.0 days	54.2 days	95.8 days

This analysis implies that shallow lakes are likely to be near saturation after a short period of circulation, but that deeper lakes may very well restratify before becoming fully reoxygenated.

5. Effects of hydrostatic pressure.

The table (15-1, Kalf) of oxygen saturation values is based on the equilibration of atmospheric oxygen with air at sea level. The saturation value for oxygen *released below the surface* (e.g. by photosynthesis) is higher because of the effect of hydrostatic pressure. The increased solubility is proportional to the hydrostatic pressure. The total pressure at depth is:

$$P_z = P_0 + 0.0967 z$$

Where: P_z is the total pressure at depth z ,
 P_0 is the atmospheric pressure at the surface, and
 z is the depth in meters.

A special case of interest is the occurrence of “*gas bubble disease*” in Columbia River fish. The supersaturation of air (both oxygen and nitrogen) is the result of entrainment of air in the water falling over the spillways of the dams. Bubbles of air are dragged down in the plunge pool to considerable depth. Some of the air in the bubbles dissolves in the water at the elevated hydrostatic pressure, leading to air supersaturation (with respect the surface of the water). Fish swimming in deeper water will equilibrate with the higher oxygen and nitrogen concentrations, but if they should subsequently swim nearer the surface, bubbles may form in their bloodstream at the reduced hydrostatic pressure. The result, particularly for small fish, can be lethal.

B. Methods to measure dissolved oxygen

1. The Winkler method. (Kalf, p226)

The Winkler method, in one of its many modifications, is the most often used chemical method to measure oxygen. The method was introduced in 1888 by L.W.Winkler. It remains the most popular and one of the most accurate methods to measure dissolved oxygen. The method involves the sequential addition of $MnSO_4$, KOH/KI , and H_2SO_4 , followed by the titration of the liberated I_2 by thiosulfate. The method is very precise (± 0.02 mg/L O_2) and accurate if done carefully. A variety of modifications are available to deal with specific chemical interferences. *A note of caution: The chemicals used in this analysis (full strength KOH and H_2SO_4) are very dangerous and must be used carefully. Any contact with these chemicals should be immediately washed off with copious amounts of water!*

2. Oxygen electrodes.

Oxygen electrodes are available which give rapid and accurate estimates of oxygen concentration. The electrodes use a thin oxygen-permeable membrane stretched over electrodes. The oxygen diffusing through the membrane is reduced with contact with the electrodes, generating a current measured by the meter. The diffusion of oxygen through the membrane is proportional to the concentration at the surface of the membrane. Accordingly, for the electrode to provide an accurate measure of oxygen in the water, the electrode requires a constant current

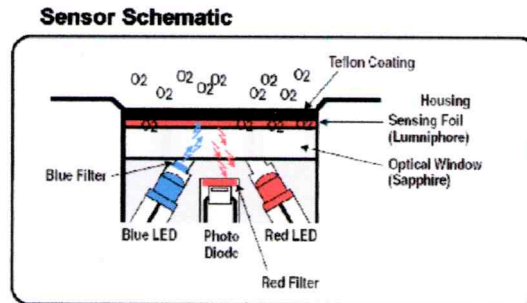
of water across the surface (best accomplished with a stir motor over the electrode). The membranes must also be replaced occasionally if damaged.

There are three fundamental techniques for measuring dissolved oxygen — galvanic, polarographic, and luminescence lifetime. Galvanic and polarographic probes use an electrode system where the dissolved oxygen reacts with the cathode to produce a current. The two probe types differ in that galvanic probes do not require an external potential (voltage), whereas polarographic probes do. Galvanic probes are more stable and more accurate at lower dissolved oxygen levels than polarographic probes. Galvanic probes often operate several months without electrolyte or membrane replacement, resulting in lower maintenance cost. Polarographic probes need to be recharged every several weeks of heavy use. These probes are often difficult to maintain. The thin Teflon membrane that covers the anode and cathode can tear, bubbles in the KCl solution bathing the anode and cathode can have bubbles in it that interfere with measurement, the probe requires constant water movement (stirring) since O₂ is being consumed by the probe during measurement

Recently, optical probes that use oxygen-dependent quenching of phosphorescence (luminescence lifetime) to measure dissolved oxygen concentration have been developed. These probes consist of a pair of blue and red light-emitting diodes (LEDs) and a silicon photodetector. These components are housed in a sensor cap that is coated with a platinum-based luminophor that is excited by light from the blue LED. The luminophor is coated on the outside with a carbon black polystyrene layer for optical insulation to prevent photobleaching of the photodetector. The probe measures the phase delay (essentially a time-delay) between the exciting blue LED and the detected red emission from the luminophor. The phase delay is inversely related to the amount of dissolved oxygen near the luminophor.

What this means to the user is that the probe:

- is highly accurate and stable,
- requires very little maintenance,
- does not require a stirring and measurement is not affected by water velocity over the probe,
- has a low power requirement, and
- a long calibration interval



Optical DO Measurements are based on selected substances that can act as dynamic fluorescence quenchers. For example for oxygen, if a ruthenium-complex is illuminated with a blue LED it is excited and emits back a red luminescent light with an intensity, or lifetime, which directly depends on the oxygen concentration. Lifetime based measurements are superior for both long-term (no drift) and fast response applications.

Table 3. ACT Evaluation – Summary of Results

Parameter	Winkler Titration	Optical DO	Polarographic	Galvanic	
Average Initial Error, mg/L (net bias)	–	0.19	0.55	0.22	} How accurate was it at the beginning?
Frequency of Initial Errors 0.2 mg/L or Less	–	50%	40%	10%	
Frequency of Initial Errors 2.0 mg/L or More	–	0%	10%	60%	
Instrumental Spread at start of tests, mg/L		0.9	3.1	9.5	} Do the instruments match each other?
Individual Precision	0.22%	0.11%	0.11%	0.18%	
Typical Drift during 1 st Week, mg/L	–	0.39	0.77	1.01	} How bad was the drift?
Variability of Drift (worst up – worst down), mg/L	–	0.58	3.94	0.74	
Earliest time any sensor drifted more than 2.0 mg/L	–	14 days	3 days	8 days	

Because of its accuracy, particularly at low dissolved oxygen concentrations, the Winkler method is typically used to calibrate dissolved oxygen meters of all types.

C. Distribution patterns.

1. Processes which affect oxygen concentration.

Equilibration with the atmosphere at the surface is a primary influence on the local concentration of oxygen. If a lake circulates freely for sufficient time, the oxygen concentration in the water column will be in equilibrium with the atmosphere (for the appropriate atmospheric pressure, or altitude, and for the temperature of the water column).

Oxygen may be *produced by photosynthesis*, leading to increased oxygen concentration. Photosynthesis may produce local super-saturation.

Oxygen may be *consumed by a variety of chemical and biochemical oxidation-reduction (redox) processes*.

Examples: Chemical oxidation of Fe⁺² to Fe⁺³ and concomitant reduction of O₂
 Oxidation of methane by bacteria and concomitant reduction of O₂
 (*Many other examples will be discussed in the context of redox processes.*)

2. Patterns observed.

The vertical pattern of oxygen concentration depends on the net effect of the processes of equilibration, production and consumption. The commonly observed patterns are:

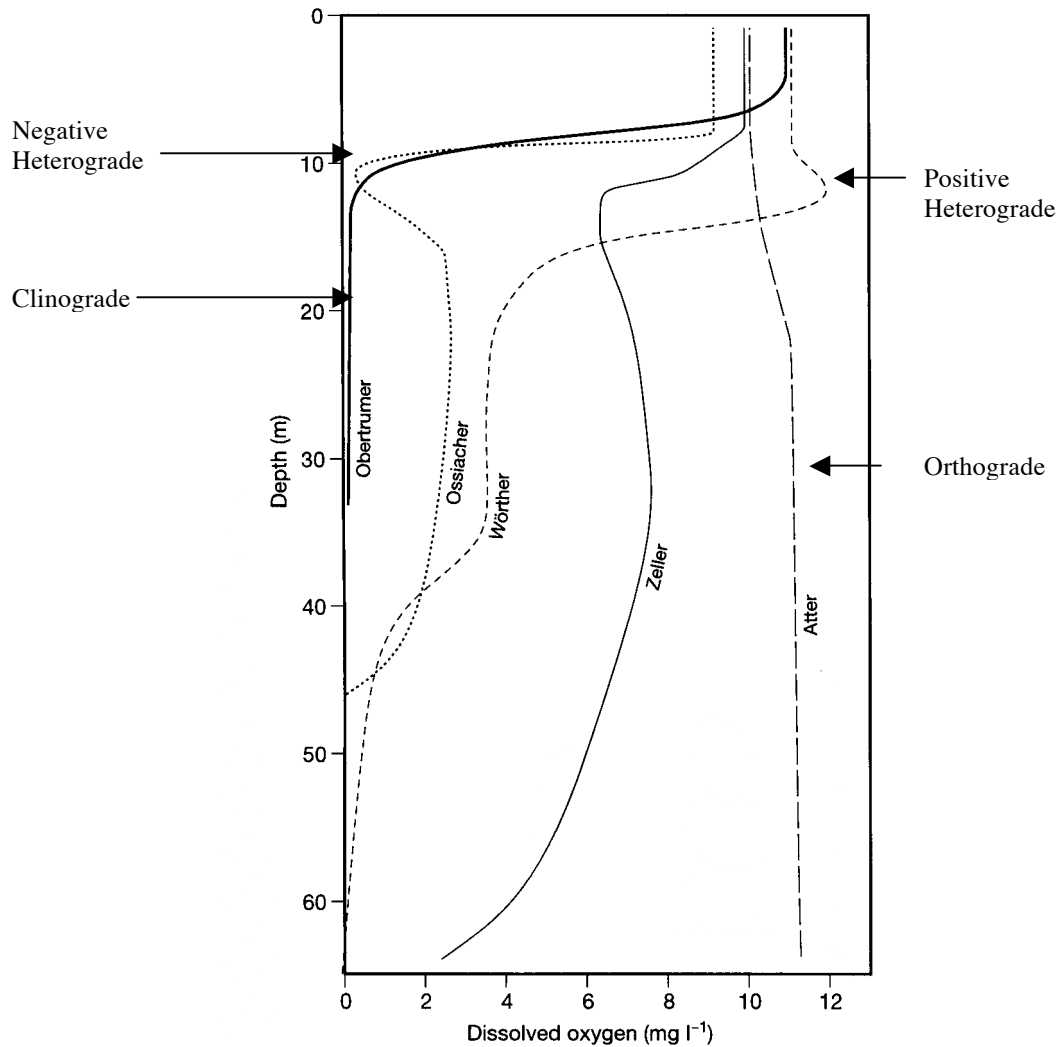


Figure 15-6 End-of-summer dissolved oxygen profiles in five Austrian lakes. (Modified after Findenegg 1967.)

a. Orthograde oxygen curve.

An *orthograde oxygen curve* is the result of physical processes alone. In a very unproductive lake, the dominant process affecting the concentration of oxygen in the water column is equilibration with the atmosphere. The curve which results after the onset of thermal stratification is the result of equilibration of the hypolimnion with the atmosphere during spring overturn followed by equilibration of the epilimnion with the atmosphere following the onset of stratification. The observed pattern (lower concentration in the epilimnion, higher in the hypolimnion) is the result of the effect of temperature on solubility.

b. Clinograde oxygen curve.

A *clinograde oxygen curve* is the result of an excess of oxygen consuming processes in the lake. Because the epilimnion remains in contact with the atmosphere, it remains at or near saturation with respect to the atmosphere. (Indeed, there may actually be an excess of production of oxygen in the epilimnion by photosynthesis.) In contrast, the hypolimnion, without contact with the atmosphere following stratification may gradually lose oxygen because of oxygen consuming redox processes, including the aerobic oxidation of organic matter raining down from photosynthesis in the epilimnion. There are a number of other potential sources of oxygen demand in the hypolimnion, including the advection of low oxygen ground water, or even anoxic ground water containing reduced chemicals such as Fe^{+2} . A clinograde oxygen curve is often observed in more productive lakes.

c. Heterograde oxygen curve (positive or negative).

Oxygen curves may also be *heterograde*. A zone of excess oxygen below the surface, often in the thermocline, may result if the water column is sufficiently transparent to permit photosynthesis in the thermocline. The oxygen produced in the thermocline may accumulate because of the inhibition of vertical mixing imposed by the temperature stratification. In this case, the oxygen curve is said to be a *positive heterograde oxygen curve*. A large metalimnetic population of phytoplankton or attached macrophytes are possible if water transparency is sufficient.

A *negative heterograde oxygen curve* is also possible. A zone of depletion may occur in the metalimnion if there is an excess of oxygen consumption processes. The diffusion of oxygen from above or below is inhibited by the temperature stratification. In contrast to a positive heterograde oxygen curve, a negative heterograde curve is likely if the water transparency is insufficient to permit net photosynthesis in the stratified layer. An excess of exposed sediment at the depth of stratification may be the cause of an excess of consumption due to the populations of benthic organisms and bacteria associated with the sediment.

3. Areal oxygen deficit. (see VHOD, p231 and AHOD, p235, Kalff.)

A clinograde oxygen curve implies an excess of consumption of oxygen in the hypolimnion. Such an excess is often simply the result of the oxidation of organic material produced in the epilimnion by phytoplankton and macrophytes. Accordingly, the amount of the deficit can provide a rough estimate of the accumulated primary production in the epilimnion during the summer stratification. Thus, the areal oxygen deficit is an estimate of the relative productivity of a lake.

The *areal oxygen deficit* may be calculated by subtracting the observed oxygen concentration observed in each successive layer of the metalimnion and hypolimnion from the oxygen concentration expected from the prevailing temperature (assuming the water was in equilibrium with the atmosphere at the time of spring circulation). The deficit of each of the successive layers is summed to give a deficit for the entire water column. Such a deficit is usually then reported on a per m^2 basis. In effect, the oxygen deficit is estimated by subtracting

the observed clinograde oxygen curve from what would be the orthograde oxygen curve is there were no consumption of oxygen.

4. Miscellaneous topics.

Patterns of oxygen concentration vs. depth in meromictic or oligomictic lakes can be very different. It is commonly the case that the monimolimnion of a meromictic lake is anaerobic. Similarly, oxygen is often missing from the hypolimnion of a tropical lake. A notable example is Lake Tanganyika. The occasional vertical mixing which occurs during brief periods of unusually cool weather may be insufficient to overcome the accumulated oxygen deficit.

In addition to the depletion of oxygen, reduced gases such as H_2S or methane can also accumulate to concentrations well above saturation with respect to atmospheric pressure (hydrostatic effect) if vertical circulation is infrequent.