

The Oxidation Potential of Oxygen and Chlorine Dioxide

From [MMS Wiki, Facts of Safety](#):

- Chlorine dioxide (ClO₂) has an oxidation potential of .95 volts, which is the weakest of all the oxidizers that are ever used in the human body. For your reference, Oxygen (O₂) has an oxidation potential of 1.28 volts.

Unfortunately this statement is incorrect. Why? The values 0.95 and 1.28 V are so called **standard** (redox) **potentials**, E° . The numerical value of the standard potential is always associated with a particular chemical equation. It also depends on the physical state of the reactants. Standard potential of oxygen will therefore be (slightly) different for the reaction of oxygen in the gas phase and that of oxygen dissolved in water. According to international convention, the reactions are always written as



ie. oxidants (substances that accept electrons, in another words, are reduced) are always on the left side of the equation.

The standard potential E° is defined as the redox potential of a solution in which the activity* of the reactants is equal to units. E° values always refer to the standard hydrogen electrode potential at which the reaction $2 \text{H}_3\text{O}^+ + 2 e^- = \text{H}_2(\text{g}) + 2 \text{H}_2\text{O}$ takes place. The potential of this electrode is defined to be **zero**. In a case that hydrogen ions H^+ take part in the reaction, E° corresponds to the redox ability of the system in solutions of **pH = 0**.

E° values of various redox reactions are tabulated. CRC Handbook of Chemistry & Physics, 88th edition, includes following equations and the corresponding standard potentials:



Symbol ClO₂(aq) in the first equation indicates that the chlorine dioxide is in solution.

Please note that in the reaction (2), only one electron is involved. The standard potential $E^\circ = 0.954 \text{ V}$ thus applies solely to the reduction of chlorine dioxide to chlorite.

So far, it seems that everything is OK. The values from CRC Handbook only slightly differ from those reported on MMS Wiki. The problem is that the E° are valid for **pH = 0**. But the human body (with the exception of the stomach) is neutral or even slightly basic. Eg. pH of blood and many other body fluids is maintained within a very narrow range of pH, around 7.40 (from 7.31 to 7.42). Therefore, in fields such as hydrochemistry, geochemistry and biochemistry, it is useful to convert standard potentials to pH = 7. These so-called **formal potentials**, $E^{\circ f}$, are in these disciplines more comparable with actual conditions than standard potentials

Regarding the pH, for the reaction



the relationship

$$E^{\circ f} = E^\circ - 2.303 \text{ RT/F} \cdot a/z \cdot \text{pH} \quad (5)$$

can be derived from the [Nernst equation](#), where

R - The ideal gas constant (8.314 J / K.mol)

T - Temperature in Kelvins (temperature in °C + 273.15)

F - Faraday's constant (96.485 C/mol)

a - The number of protons H^+ in reaction

z - Number of e^- electrons exchanged

For the temperature of 36.5 °C and pH = 7.4 we get

$$E^{\circ f} = E^\circ - 0.455 a/z \quad (6)$$

If the H^+ protons are not involved in the reaction, as it is in the case of chlorine dioxide reduction to chlorite (eq. 2), $a = 0$ and $E^{\circ f} = E^\circ$, ie. the formal potential is pH independent. But it is quite different in the case of reduction of oxygen (eq. 3), where $a = 4$, $z = 4$, $a/z = 4/4 = 1$, then

$$E^{\circ f} = E^\circ - 0.455 = 1.229 - 0.455 = \mathbf{0.774 \text{ V}}$$

* Activity - at very low concentrations is equal to the concentration of the substance

Standard and formal potentials for reactions with more than one electron transfer (that is reduction of chlorine dioxide, chlorite and chlorous acid to chloride) are filled in next table:

Reaction	Standard potential E° [V] pH = 0; t = 25 °C	Formal potential $E^{\circ f}$ [V] pH = 7.4; t = 36,5 °C	$E^{\circ f}$ difference $\text{ClO}_2 - \text{O}_2$	
			[V]	[%]
$\text{O}_2 + 4 \text{H}^+ + 4 \text{e}^- = 2 \text{H}_2\text{O}$	1.229	0.774		
$\text{ClO}_2(\text{aq}) + \text{e}^- = \text{ClO}_2^-$	0.954	0.954	+0.18	+23
$\text{ClO}_2 + 4 \text{H}^+ + 5 \text{e}^- = \text{Cl}^- + 2 \text{H}_2\text{O}$	1.51	1.15	+0.38	+49
$\text{ClO}_2^- + 4 \text{H}^+ + 4 \text{e}^- = \text{Cl}^- + 2 \text{H}_2\text{O}$	1.59	1.14	+0.37	+47
$\text{HClO}_2 + 3 \text{H}^+ + 4 \text{e}^- = \text{Cl}^- + 2 \text{H}_2\text{O}$	1.570	1.23	+0.46	+59

It can be clearly seen that **under physiological conditions:**

- **the formal oxidation potential of oxygen, 0.774, is markedly lower than that of the chlorine dioxide, chlorite or chlorous acid;**
- standard potential 0.954 V is valid for one electron reduction of chlorine dioxide to chlorite only;
- if more than one electron is exchanged, formal oxidation potentials of chlorine dioxide, chlorite and chlorous acid are substantially higher (by 49-59 %) than that of oxygen.

In contrast to oxygen, therefore, chlorine dioxide can readily react with certain amino acids (e.g. cysteine, tryptophan and tyrosine), lipids, and other biological materials. From this perspective, one can not claim that the use of MMS/CDS is completely safe. Possible adverse side effects can not be ruled out.