Water & Wastewater Treatment-2

- Chemical Oxidation

(from *MWH's Water Treatment Principles and Design* by Crittenden et al.)

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Definition of Reduction and Oxidation

√ Definition of reduction & oxidation reactions (i.e., redox reactions)

- Oxidation: loss of e^- or H, gain of O, increase of oxidation number
- Reduction: gain of e^- or H, loss of O, decrease of oxidation number

e.g., $C + H_2 \rightarrow CH_4$

$C + O_2 \rightarrow CO_2$

$Fe^0 \rightarrow Fe^{2+} + 2e^-$

e.g., $O_2 + H_2 \rightarrow H_2O_2$

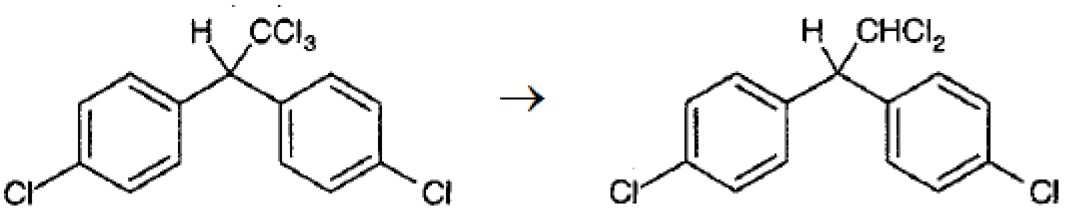
$O_2 + 2e^- + 2H^+ \rightarrow H_2O_2$

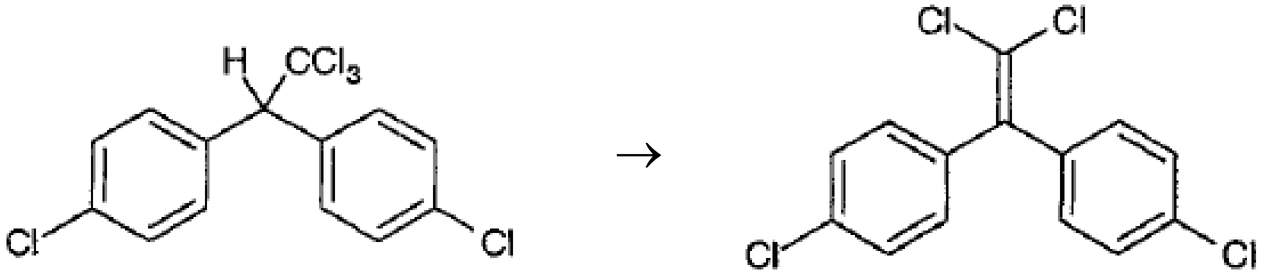
e.g., $O_2 + 2H_2 \rightarrow 2H_2O$

$O_2 + 4e^- + 4H^+ \rightarrow 2H_2O$

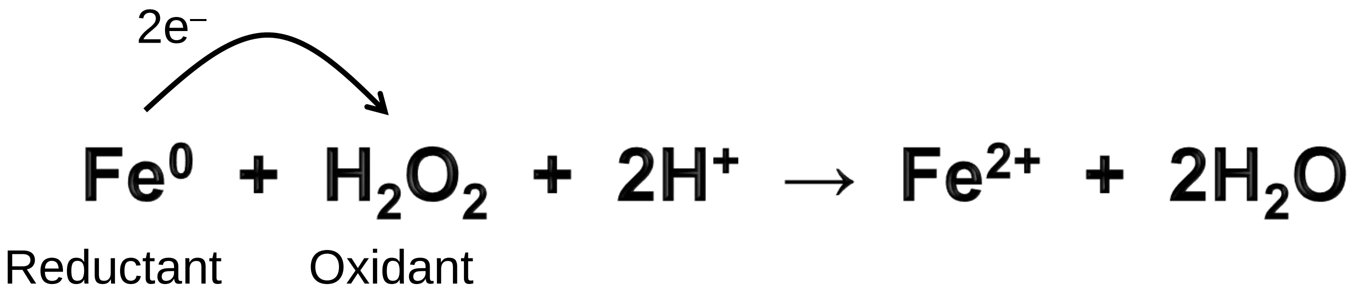
Oxidation number

How about this?





Oxidant and Reductant



2e⁻

$$\mathrm{Fe^0 + H_2O_2 + 2H^+ \rightarrow Fe^{2+} + 2H_2O}$$

Reductant Oxidant

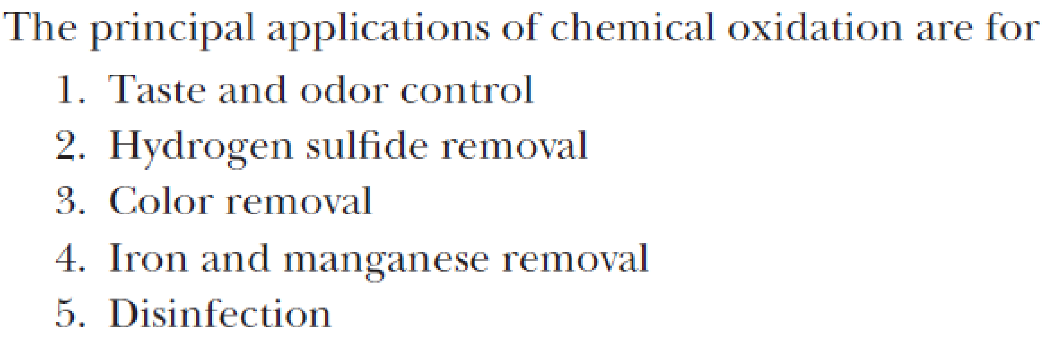
$$\text{Half Reactions}\left\{\begin{array}{l}\mathrm{Fe^0 \rightarrow Fe^{2+} + 2e^-} \\ \mathrm{H_2O_2 + 2e^- + 2H^+ \rightarrow 2H_2O}\end{array}\right.$$

Oxidation Processes for Water Treatment

Commonly Used Oxidants

1. Chlorine
2. Ozone
3. Chlorine dioxide
4. Permanganate
5. Hydrogen peroxide

Application of Conventional Oxidants in Water Treatment



The principal applications of chemical oxidation are for

1. Taste and odor control
2. Hydrogen sulfide removal
3. Color removal
4. Iron and manganese removal
5. Disinfection
6. Organic contaminants

Table

Oxidants and their applications in water treatment

Purpose	Oxidants	Applications
Oxidation of reduced inorganic species	Chlorine, hydrogen peroxide, permanganate, chlorine dioxide	Convert soluble metals such as Fe(II) and Mn(II) to insoluble forms; oxidize odorous sulfide; destroy metal organic complexes
Oxidation of organics	Ozone, AOPs, ultraviolet light, permanganate, chlorine dioxide	Destroy taste- and odor-causing compounds; destroy toxic organics [e.g., pesticides, benzene, trichloroethene, methyl tertiary-butyl ether (MTBE)]; eliminate color; reduce natural organic matter and disinfection by-product precursors
Coagulation aids	Ozone	Reduce amount of coagulant and/or improve coagulation process
Biocidal agents	Ozone, chlorine, iodine, ultraviolet light	Control nuisance growths such as algae in pretreatment basins or reservoirs; as primary disinfectants to meet *Ct*[a] regulations

[a] *Ct* = product of oxidant residual concentration (mg/L) and contact time (min).

✓ TASTE AND ODOR CONTROL

- In surface water: originated from algal bloom
  e.g., Geosmin, 2-Methylisoborneol (2-MIB)

- Threshold odor concentration: 4 ng/L for geosmin, 9 ng/L for 2-MIB

- In groundwater: sulfides (hydrogen sulfide and organic sulfides)
  Production of polysulfides (oxidation byproducts, usually S_8, generates turbidity) is a problem when H_2S > 1 ppm

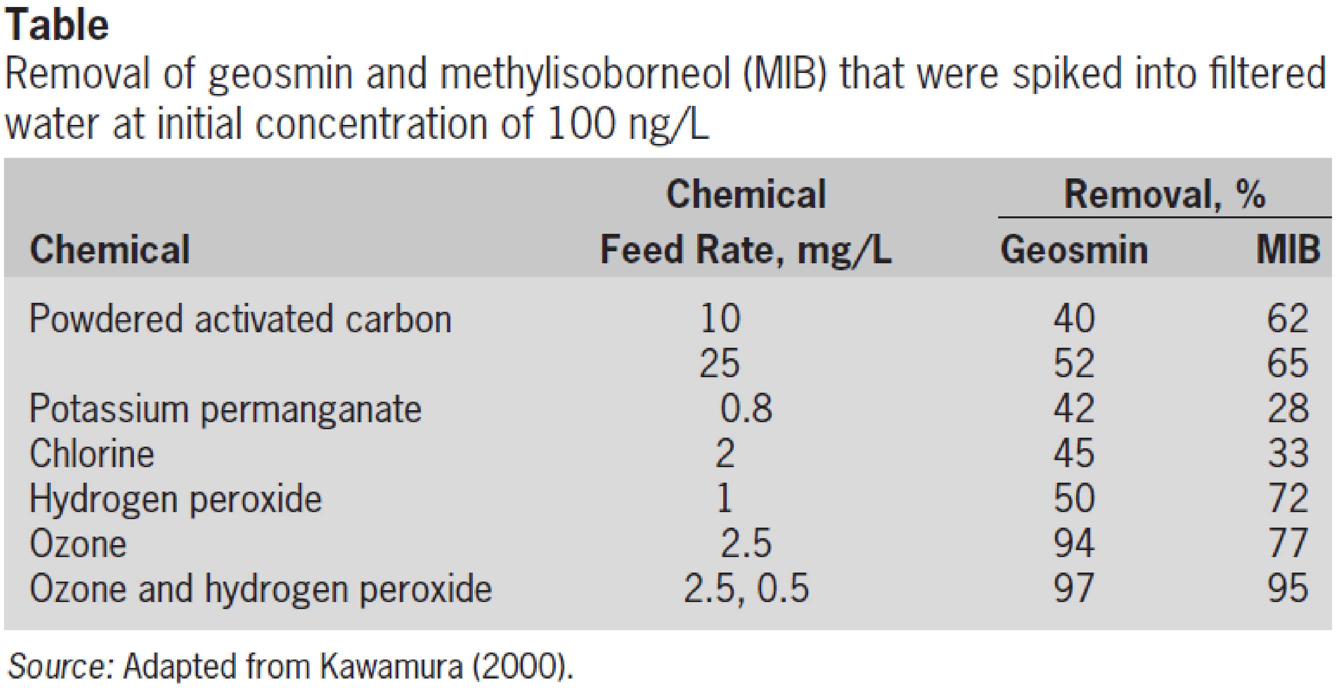
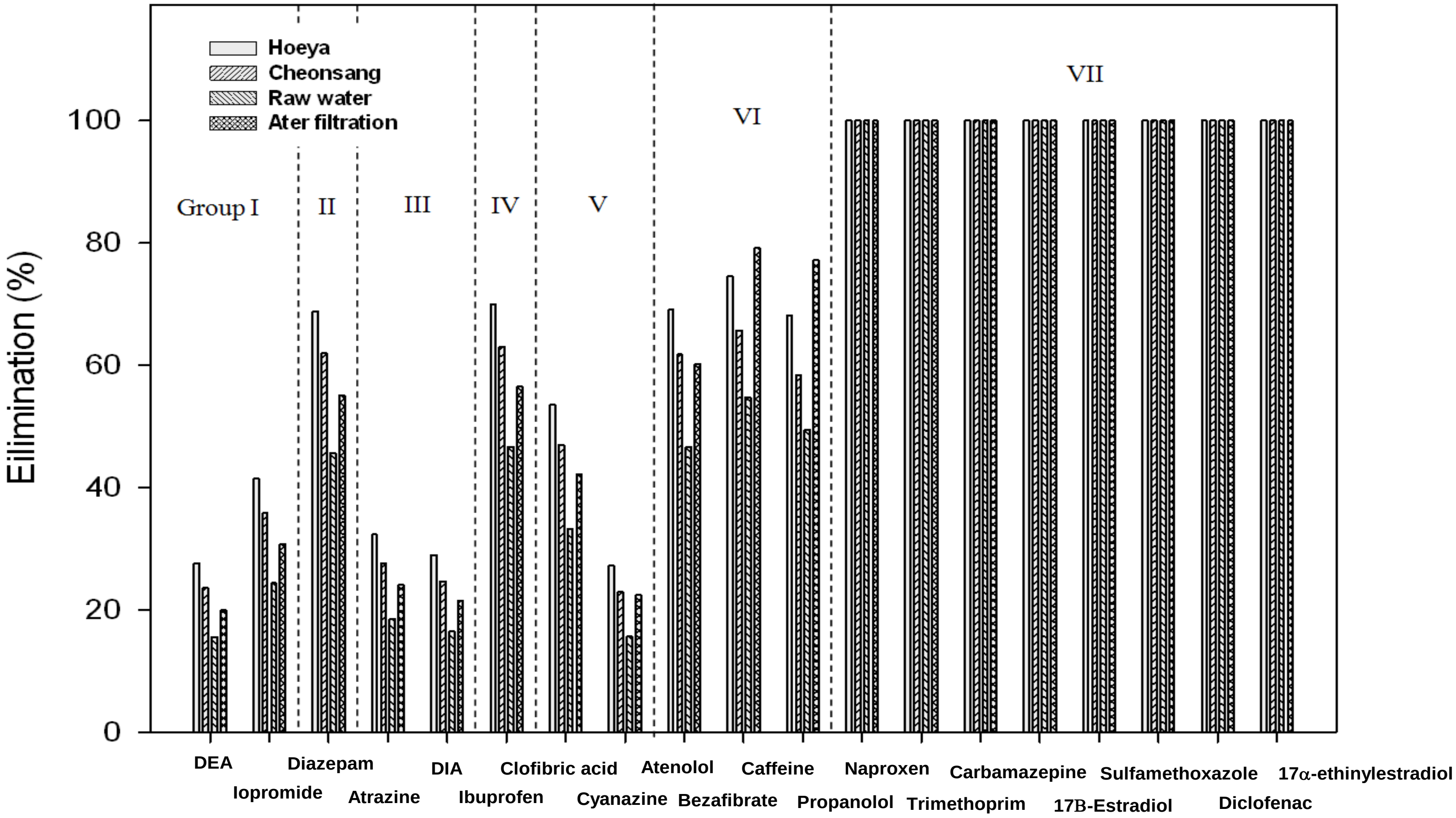


Table
Removal of geosmin and methylisoborneol (MIB) that were spiked into filtered water at initial concentration of 100 ng/L

Chemical	Chemical Feed Rate, mg/L	Removal, % Geosmin	Removal, % MIB
Powdered activated carbon	10	40	62
	25	52	65
Potassium permanganate	0.8	42	28
Chlorine	2	45	33
Hydrogen peroxide	1	50	72
Ozone	2.5	94	77
Ozone and hydrogen peroxide	2.5, 0.5	97	95

Source: Adapted from Kawamura (2000).

- ✓ **COLOR REMOVAL**
- ✓ **OXIDATION AS A COAGULATION AID**
- ✓ **IRON AND MANGANESE REMOVAL**
- ✓ **OXIDATION OF SELECTED TRACE ORGANIC CONSTITUENTS**



Predicted oxidation of grouped organic pollutants in 1 ppm of ozone dose

Fundamentals of Oxidation and Reduction

Introduction to Redox Reactions

✓ **Definitions of oxidation and reduction**

✓ **Half Reactions**

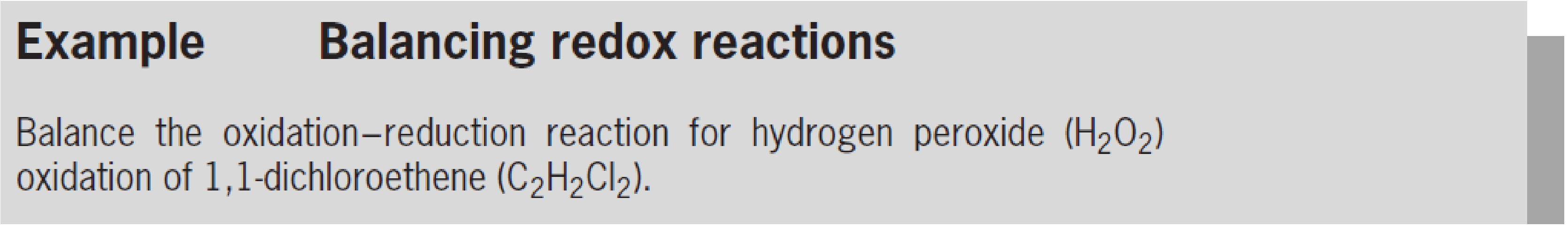
$$Mn^{2+} + O_3(aq) + H_2O \rightarrow MnO_2(s) + O_2(aq) + 2H^+$$

⬇

$$Mn^{2+} + 2H_2O \rightarrow MnO_2(s) + 4H^+ + 2e^- \qquad \text{(oxidation)}$$

$$O_3(aq) + 2H^+ + 2e^- \rightarrow O_2(aq) + H_2O \qquad \text{(reduction)}$$

✓ **Balancing Redox Reactions**

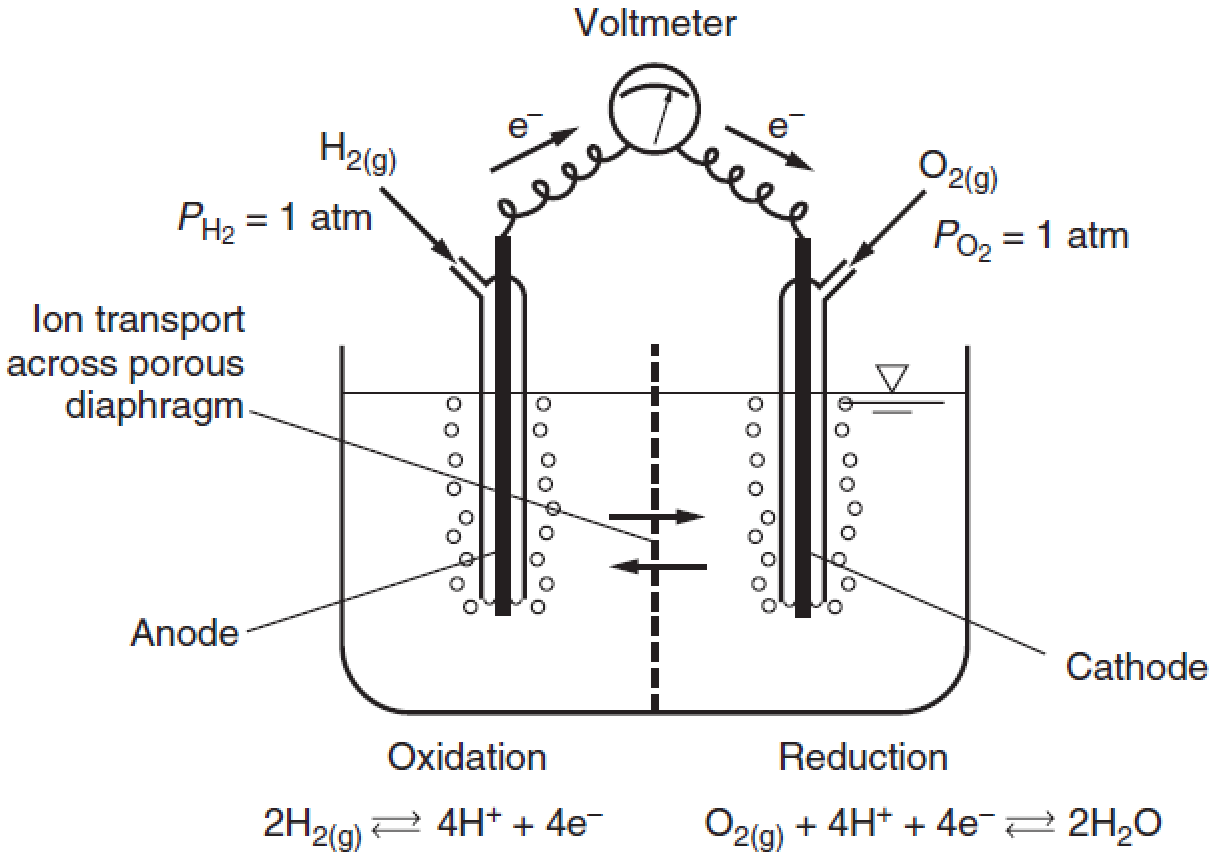


Example **Balancing redox reactions**

Balance the oxidation–reduction reaction for hydrogen peroxide (H_2O_2) oxidation of 1,1-dichloroethene ($C_2H_2Cl_2$).

- ✓ **Define final products (make an unbalanced equation with them)**
- ✓ **Balance atoms and charge (Use H^+, OH^- or H_2O if necessary)**

Standard Redox Potential



$$O_2\,(aq) + 4H^+ + 4e^- \rightleftarrows 2H_2O \qquad \text{(reduction)} \qquad E^\circ_{red} = 1.27\ \text{V}$$

$$H_2 \rightleftarrows 2H^+ + 2e^- \qquad \text{(oxidation)} \qquad E^\circ_{ox} = 0\ \text{V}$$

Expression of Redox Potential

√ "Reduction (redox) potential" is not for a compound, but for a reaction (or a redox couple)!

e.g.,

The reduction potential of A^{3+} is ??? V_{SHE} **X**

Because A^{3+} may go through different redox reactions with different reduction potentials.

$$A^{3+} + e^{-} \rightarrow A^{2+}$$
$$A^{3+} + 3e^{-} \rightarrow A^{0}$$

The reduction potential of $A^{3+} + e^{-} \rightarrow A^{2+}$ is ??? V_{SHE} **O**

The reduction potential of A^{3+}/A^{2+} is ??? V_{SHE} **O**

$E^{o}[A^{3+}/A^{2+}]$ = ??? V_{SHE} **O**

Standard Redox Potentials for Several Oxidants

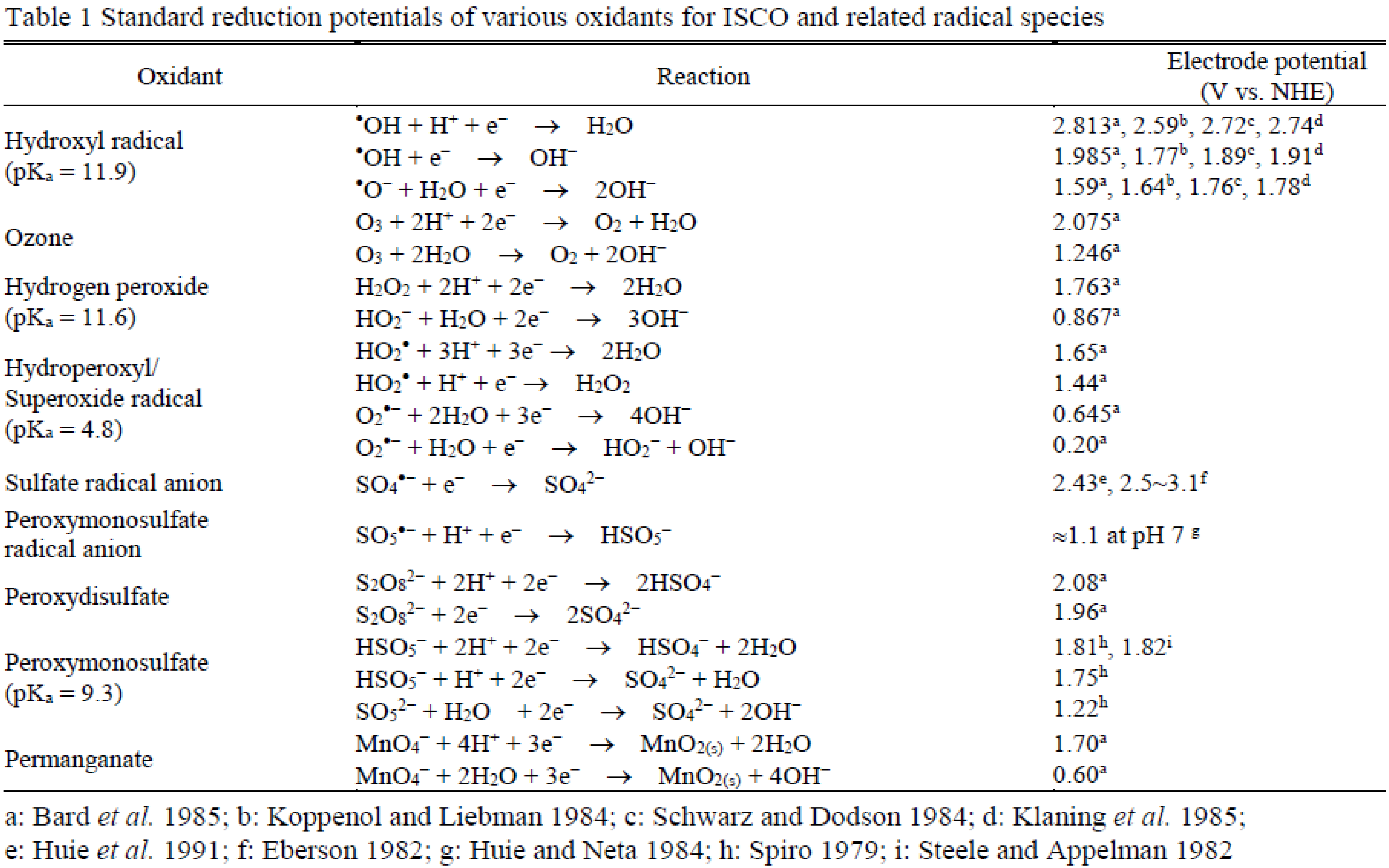


Table 1 Standard reduction potentials of various oxidants for ISCO and related radical species

Oxidant	Reaction	Electrode potential (V vs. NHE)
Hydroxyl radical (pK$_a$ = 11.9)	$^{\bullet}\mathrm{OH} + \mathrm{H}^+ + e^- \rightarrow \mathrm{H_2O}$	2.813[a], 2.59[b], 2.72[c], 2.74[d]
	$^{\bullet}\mathrm{OH} + e^- \rightarrow \mathrm{OH}^-$	1.985[a], 1.77[b], 1.89[c], 1.91[d]
	$^{\bullet}\mathrm{O}^- + \mathrm{H_2O} + e^- \rightarrow 2\mathrm{OH}^-$	1.59[a], 1.64[b], 1.76[c], 1.78[d]
Ozone	$\mathrm{O_3} + 2\mathrm{H}^+ + 2e^- \rightarrow \mathrm{O_2} + \mathrm{H_2O}$	2.075[a]
	$\mathrm{O_3} + 2\mathrm{H_2O} \rightarrow \mathrm{O_2} + 2\mathrm{OH}^-$	1.246[a]
Hydrogen peroxide (pK$_a$ = 11.6)	$\mathrm{H_2O_2} + 2\mathrm{H}^+ + 2e^- \rightarrow 2\mathrm{H_2O}$	1.763[a]
	$\mathrm{HO_2}^- + \mathrm{H_2O} + 2e^- \rightarrow 3\mathrm{OH}^-$	0.867[a]
Hydroperoxyl/ Superoxide radical (pK$_a$ = 4.8)	$\mathrm{HO_2}^{\bullet} + 3\mathrm{H}^+ + 3e^- \rightarrow 2\mathrm{H_2O}$	1.65[a]
	$\mathrm{HO_2}^{\bullet} + \mathrm{H}^+ + e^- \rightarrow \mathrm{H_2O_2}$	1.44[a]
	$\mathrm{O_2}^{\bullet-} + 2\mathrm{H_2O} + 3e^- \rightarrow 4\mathrm{OH}^-$	0.645[a]
	$\mathrm{O_2}^{\bullet-} + \mathrm{H_2O} + e^- \rightarrow \mathrm{HO_2}^- + \mathrm{OH}^-$	0.20[a]
Sulfate radical anion	$\mathrm{SO_4}^{\bullet-} + e^- \rightarrow \mathrm{SO_4}^{2-}$	2.43[e], 2.5~3.1[f]
Peroxymonosulfate radical anion	$\mathrm{SO_5}^{\bullet-} + \mathrm{H}^+ + e^- \rightarrow \mathrm{HSO_5}^-$	≈1.1 at pH 7 [g]
Peroxydisulfate	$\mathrm{S_2O_8}^{2-} + 2\mathrm{H}^+ + 2e^- \rightarrow 2\mathrm{HSO_4}^-$	2.08[a]
	$\mathrm{S_2O_8}^{2-} + 2e^- \rightarrow 2\mathrm{SO_4}^{2-}$	1.96[a]
Peroxymonosulfate (pK$_a$ = 9.3)	$\mathrm{HSO_5}^- + 2\mathrm{H}^+ + 2e^- \rightarrow \mathrm{HSO_4}^- + 2\mathrm{H_2O}$	1.81[h], 1.82[i]
	$\mathrm{HSO_5}^- + \mathrm{H}^+ + 2e^- \rightarrow \mathrm{SO_4}^{2-} + \mathrm{H_2O}$	1.75[h]
	$\mathrm{SO_5}^{2-} + \mathrm{H_2O} + 2e^- \rightarrow \mathrm{SO_4}^{2-} + 2\mathrm{OH}^-$	1.22[h]
Permanganate	$\mathrm{MnO_4}^- + 4\mathrm{H}^+ + 3e^- \rightarrow \mathrm{MnO_{2(s)}} + 2\mathrm{H_2O}$	1.70[a]
	$\mathrm{MnO_4}^- + 2\mathrm{H_2O} + 3e^- \rightarrow \mathrm{MnO_{2(s)}} + 4\mathrm{OH}^-$	0.60[a]

a: Bard *et al.* 1985; b: Koppenol and Liebman 1984; c: Schwarz and Dodson 1984; d: Klaning *et al.* 1985;
e: Huie *et al.* 1991; f: Eberson 1982; g: Huie and Neta 1984; h: Spiro 1979; i: Steele and Appelman 1982

Source: Lee et al., 2019 (*Membr. Wat. Treat.*)

Redox Potential and Thermodynamics

√ We can tell if a certain redox reaction is thermodynamically favored or not by reduction (redox) potentials of its half reactions!

e.g.,

$Ni^0 + Fe^{2+} \rightarrow Ni^{2+} + Fe^0$ (favored or unfavored) ?

$Fe^{2+} + 2e^- \rightarrow Fe^0 \quad E^o = -0.44\ V_{SHE}$

$Ni^{2+} + 2e^- \rightarrow Ni^0 \quad E^o = -0.20\ V_{SHE}$

$Fe^0 + 2H^+ \rightarrow Fe^{2+} + H_2$ (favored or unfavored) ?

$H^+ + 2e^- \rightarrow H_2 \quad E^o = 0\ V_{SHE}$

$Fe^{2+} + 2e^- \rightarrow Fe^0 \quad E^o = -0.44\ V_{SHE}$

Redox Potential and Thermodynamics

e.g.,

$Ni^0 + Fe^{2+} \rightarrow Ni^{2+} + Fe^0$ (favored or unfavored) ?

$Fe^{2+} + 2e^- \rightarrow Fe^0 \quad E^{o(1)} = -0.44\ V_{SHE}$

$Ni^0 \rightarrow Ni^{2+} + 2e^- \quad E^{o(2)} = +0.20\ V_{SHE}$

$E^o_{Rxn} = E^{o(1)} + E^{o(2)} = -0.24$

$Fe^0 + 2H^+ \rightarrow Fe^{2+} + H_2$ (favored or unfavored) ?

$H^+ + 2e^- \rightarrow H_2 \quad E^{o(1)} = 0\ V_{SHE}$

$Fe^0 \rightarrow Fe^{2+} + 2e^- \quad E^{o(2)} = +0.44\ V_{SHE}$

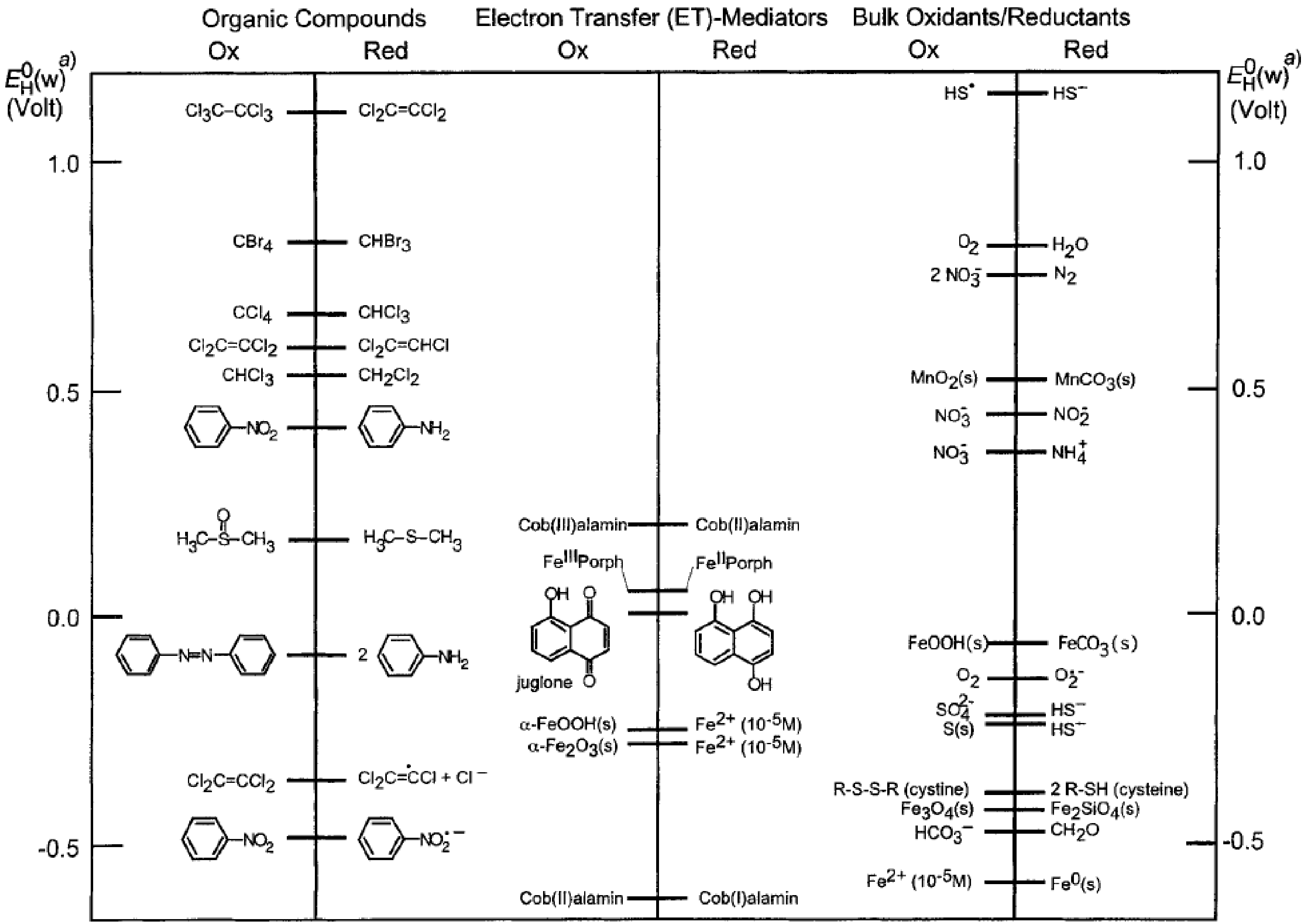
$E^o_{Rxn} = E^{o(1)} + E^{o(2)} = +0.44$

$\Delta G^\circ = -nFE^\circ$

$E^o_{Rxn} > 0$ Thermodynamically favored

$E^o_{Rxn} < 0$ Thermodynamically unfavored

Redox Potential and Thermodynamics



a) pH = 7; $[HCO_3^-] = [Cl^-] = 10^{-3}$ M; $[Br^-] = 10^{-5}$ M

Redox Potentials of Combined Reactions

e.g.,

$$A^{3+} + 2e^{-} \rightarrow A^{+} \quad E^{o(1)} = +0.4\ V_{SHE}$$

$$A^{+} + e^{-} \rightarrow A^{0} \quad E^{o(2)} = +0.2\ V_{SHE}$$

$$A^{3+} + 3e^{-} \rightarrow A^{0} \quad E^{o(3)} = ?$$

$$-\left(n_{\text{ox},1} + n_{\text{ox},2}\right) F E^{\circ}_{\text{ox,sum}} = -n_{\text{ox},1} F E^{\circ}_{\text{ox},1} - n_{\text{ox},2} F E^{\circ}_{\text{ox},2}$$

$$E^{\circ}_{\text{ox,sum}} = \frac{n_{\text{ox},1} E^{\circ}_{\text{ox},1} + n_{\text{ox},2} E^{\circ}_{\text{ox},2}}{n_{\text{ox},1} + n_{\text{ox},2}}$$

$$E^{\circ}_{\text{red,sum}} = \frac{n_{\text{red},1} E^{\circ}_{\text{red},1} + n_{\text{red},2} E^{\circ}_{\text{red},2}}{\mathrm{n}_{\text{red},1} + \mathrm{n}_{\text{red},2}}$$

$$E^{o(3)} = 2E^{o(1)} + E^{o(2)} / (2 + 1) = (2x0.4 + 0.2)/3 = 0.33\ V_{SHE}$$

Example Oxidation of bromide to bromate

Determine the oxidation potential for converting bromide (Br^-) to bromate (BrO_3^-) from the hypobromous/bromide acid reaction and bromate/hypobromous reaction.

Solution

1. From Table E1 at the website listed in in App. E, determine the two half reactions, their potentials, and the overall reaction:

$$\begin{array}{rll}
Br^- + H_2O \rightleftarrows HOBr + H^+ + 2e^- & \text{(oxidation)} & E^\circ_{ox} = -1.33\ \text{V} \\
HOBr + 2H_2O \rightleftarrows BrO_3^- + 5H^+ + 4e^- & \text{(oxidation)} & E^\circ_{ox} = -1.49\ \text{V} \\
\hline
Br^- + 3H_2O \rightleftarrows BrO_3^- + 6H^+ + 6e^- & \text{(oxidation)} & E^\circ_{ox,sum} = ?
\end{array}$$

2. Determine the potential for the oxidation reaction using Eq. 8-20 and the values from the online table of standard redox potentials

pH–Dependence of Redox Potential

??? + ne$^-$ + mH$^+$ → ???

E_{red} (at specific pH) – $E_{\text{red}}^{\text{o}}$ (pH =0)

$$\Delta E^\circ_{\text{red}} = -\left(\frac{2.303RT}{nF}\right)\log\left(\frac{1}{[\text{H}^+]^{\text{m}}}\right)$$

$$= -\left[\frac{(2.303)\,(8.314\ \text{J/mol}\cdot\text{K})\,(298\ \text{K})}{(96{,}500\ \text{C/eq})\,(n\ \text{eq/mol})}\right]^{\text{m}}\text{pH}$$

$$= -\left(\frac{0.0591}{n}\right)^{\text{m}}\times\text{pH}$$

$\Delta G_{\text{r}} = \Delta G_{\text{r}}^{\text{o}} + RT\ lnQ_r$

$-nFE_{\text{red}} = -nFE_{\text{red}}^{\text{o}} + RT\ lnQ_r$

$E_{\text{red}} - E_{\text{red}}^{\text{o}} = -RT/nF\ lnQ_r$

$E_{\text{red}} - E_{\text{red}}^{\text{o}} = -2.303RT/nF\ \log(1/[\text{H}^+]^{\text{m}})$

E_H–pH Predominance Area Diagrams: Definition and Example for Chlorine

✓ OXYGEN

$$O_2(g) + 4H^+ + 4e^- \rightleftarrows 2H_2O \quad E^\circ_{\text{red}} = 1.23\ \text{V}$$

$$E_H = E^\circ - \frac{0.059}{n} \log \frac{1}{[H^+]^4 P_{O_2}}$$

$$= E^\circ - \frac{0.059}{4}(4\text{pH} - \log P_{O_2})$$

where E_H = electrode potential as function of pH, V
E = standard electrode potential, V
n = number of electrons transferred, eq/mol
P_{O_2} = partial pressure of oxygen, atm

Assuming $P_{O_2} = 0.21$ atm

$$E_H = 1.24 - 0.059\text{pH}$$

✓ HYDROGEN

$$2H_2O + 2e^- \rightleftarrows H_2(g) + 2OH^- E^\circ = -0.828\ \text{V}$$ (at pH 14)

$2H^+ + 2e^- \leftrightarrow H_2(g)$ $E^\circ = 0$ V

(at pH 0)

$$E_H = E^\circ - \frac{0.059}{2}(-2\text{pOH} + \log P_{H_2})$$

Assuming $P_{H_2} = 1$ atm,

$$E_H = -0.059\text{pH}$$

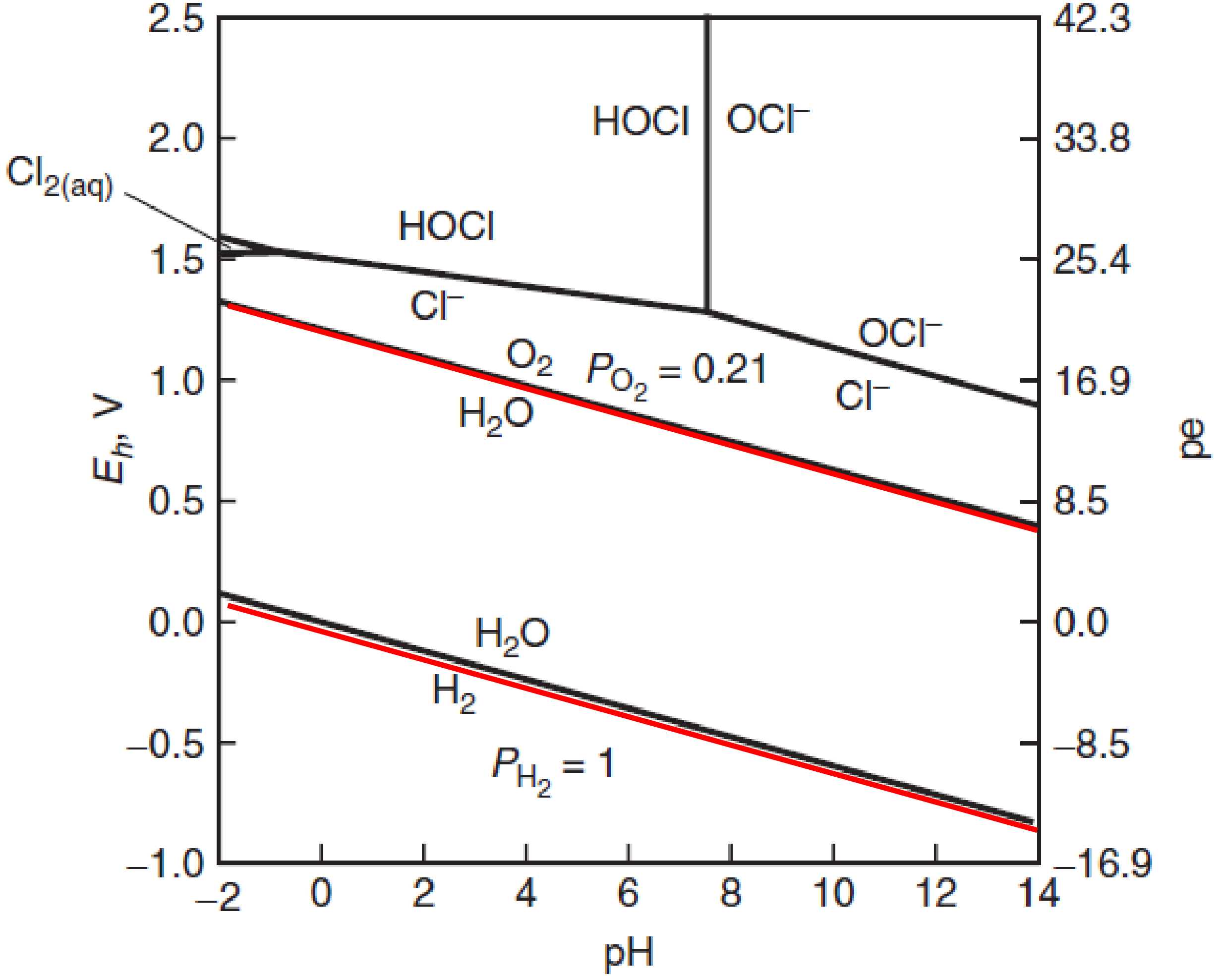


Figure
Predominance area diagram for chlorine system with total chlorine species concentration $C_{T,Cl}$ of 10^{-4} mol/L ($C_{T,Cl} = 10^{-4}$ mol/L $= 2[Cl_2(aq)] + [HOCl] + [OCl^-] + [Cl^-]$).

*pe = $-\log[e^-]$ = $F/(2.3RT)E_h$

✓ CHLORINE SPECIES

$$C_{T,\mathrm{Cl}} = 10^{-4}\ \mathrm{M} = 2[\mathrm{Cl_2(aq)}] + [\mathrm{HOCl}] + [\mathrm{OCl^-}] + [\mathrm{Cl^-}]$$

$$\mathrm{Cl_2(aq) + H_2O \rightleftarrows Cl^- + HOCl + H^+}$$

$$\mathrm{HOCl \rightleftarrows H^+ + OCl^-} \qquad \mathrm{p}K_a = 7.5 \text{ at } 25°\mathrm{C}$$

$$\mathrm{2HOCl + 2H^+ + 2e^- \rightleftarrows Cl_2\,(aq) + 2H_2O} \qquad E^\circ = 1.61\ \mathrm{V}$$

$$E_H = E^\circ - \frac{0.059}{2}\log\left\{\frac{[\mathrm{Cl_{2(aq)}}]}{[\mathrm{H^+}]^2[\mathrm{HOCl}]^2}\right\}$$

At the boundary, [HOCl] equals $[\mathrm{Cl_2(aq)}]$, and when HOCl and $\mathrm{Cl_2(aq)}$ predominate in the solution, $C_{T,\mathrm{Cl}} \approx 2[\mathrm{Cl_2(aq)}] + [\mathrm{HOCl}] = 10^{-4}$ M and $[\mathrm{HOCl}] = [\mathrm{Cl_2(aq)}] = 3.33 \times 10^{-5}$ M,

$$E_H = 1.61 - \frac{0.059}{2}\left\{2\mathrm{pH} + \log\left[\frac{3.33 \times 10^{-5}}{(3.33 \times 10^{-5})^2}\right]\right\}$$

$$= 1.47 - 0.059\ \mathrm{pH} \qquad (1)$$

$$\mathrm{Cl_2(aq)} + 2e^- \rightleftarrows 2\mathrm{Cl}^- \qquad E^\circ = 1.396\ \mathrm{V}$$

$$E_H = E^\circ - \frac{0.059}{2}\log\left(\frac{[\mathrm{Cl}^-]^2}{[\mathrm{Cl_2(aq)}]}\right)$$

Similarly, at the boundary $[\mathrm{Cl}^-]$ equals $[\mathrm{Cl_2(aq)}]$, and when Cl^- and $\mathrm{Cl_2(aq)}$ predominate in the solution, $C_{T,\mathrm{Cl}} \approx 2[\mathrm{Cl_2(aq)}] + [\mathrm{Cl}^-] = 10^{-4}$ M and $[\mathrm{Cl}^-] = [\mathrm{Cl_2(aq)}] = 3.33 \times 10^{-5}$ M,

$$E_H = 1.52\ \mathrm{V} \qquad \textbf{(2)}$$

$$\mathrm{HOCl} + \mathrm{H}^+ + 2e^- \rightleftarrows \mathrm{Cl}^- + \mathrm{H_2O}$$

The standard cell potential must be determined using the combined reactions shown below:

$$2\mathrm{HOCl} + 2\mathrm{H}^+ + 2e^- \rightleftarrows \mathrm{Cl_2(aq)} + 2\mathrm{H_2O} \qquad E^\circ_{\mathrm{red}} = 1.61\ \mathrm{V}$$

$$\mathrm{Cl_2(aq)} + 2e^- \rightleftarrows 2\mathrm{Cl}^- \qquad E^\circ_{\mathrm{red}} = 1.396\ \mathrm{V}$$

$$\mathrm{HOCl} + \mathrm{H}^+ + 2e^- \rightleftarrows \mathrm{Cl}^- + \mathrm{H_2O} \qquad E^\circ_{\mathrm{red,sum}} = ?$$

The value of $E^\circ_{\mathrm{red,sum}}$ can be computed

$$E^\circ_{\mathrm{red,sum}} = \frac{n_{\mathrm{red},1}E^\circ_{\mathrm{red},1} + n_{\mathrm{red},2}E^\circ_{\mathrm{red},2}}{n_{\mathrm{red},1} + n_{\mathrm{red},2}} = \frac{2\,(1.61\ \mathrm{V}) + 2\,(1.396\ \mathrm{V})}{2+2} = 1.50\ \mathrm{V}$$

The E_H can be determined using the expression

$$E_H = E^\circ - \frac{0.059}{2}\log\left(\frac{[\mathrm{Cl}^-]}{[\mathrm{HOCl}][\mathrm{H}^+]}\right)$$

At the boundary, $[\mathrm{Cl}^-]$ equals $[\mathrm{HOCl}]$

$$E_H = 1.50 - \frac{0.059}{2}\mathrm{pH} \qquad \textbf{(3)}$$

$$\mathrm{OCl^- + 2H^+ + 2e^- \rightleftarrows Cl^- + H_2O}$$

$$\begin{array}{lll}
\mathrm{HOCl + H^+ + 2e^- \rightleftarrows Cl^- + H_2} & \Delta G^\circ_{\mathrm{Rxn,1}} = ? & \\
\mathrm{OCl^- + H^+ \rightleftarrows HOCl} & \Delta G^\circ_{\mathrm{Rxn,2}} = ? & \\
\hline
\mathrm{OCl^- + 2H^+ + 2e^- \rightleftarrows Cl^- + H_2O} & \Delta G^\circ_{\mathrm{Rxn,sum}} = ? & E^\circ_{\mathrm{red,sum}} = ?\,\mathrm{V}
\end{array}$$

The value of $\Delta G^\circ_{\mathrm{Rxn,1}}$ for the reaction involving hypochlorous acid can be determined

$$\Delta G^\circ_{\mathrm{Rxn,HOCl}} = -nFE^\circ_{\mathrm{Rxn,1}} \quad E^\circ_{\mathrm{Rxn,1}} = 1.5\ \mathrm{V} = 1.5\ \mathrm{J/C}$$

$$= -\left(2\ \mathrm{eq/mol}\right)\left(96{,}500\ \mathrm{C/eq}\right)\left(1.5\ \mathrm{J/C}\right)$$

$$= -289{,}000\ \mathrm{J/mol}$$

The value of $\Delta G^\circ_{\mathrm{Rxn.OCl^-}}$ for the reaction involving the hypochlorite ion can be determined

$$\Delta G^\circ_{\mathrm{Rxn,OCl^-}} = -RT\ln K_{\mathrm{eq}} \quad \text{where } K_{\mathrm{eq}} = 10^{7.5} \qquad \mathrm{p}K_a = 7.5$$

$$= -\left(8.314\ \mathrm{J/mol\cdot K}\right)\left(298\ \mathrm{K}\right)\ln\left(10^{7.5}\right)$$

$$= -42{,}800\ \mathrm{J/mol}$$

The value of $\Delta G^\circ_{\mathrm{Rxn,sum}}$ can be obtained

$$\Delta G^\circ_{\mathrm{Rxn,sum}} = \Delta G^\circ_{\mathrm{Rxn,HOCl}} + \Delta G^\circ_{\mathrm{Rxn,OCl^-}}$$

$$= \left(-289{,}000\ \mathrm{J/mol}\right) + \left(-42{,}800\ \mathrm{J/mol}\right)$$

$$= -331{,}800\ \mathrm{J/mol}$$

The value of $E^\circ_{\text{red,sum}}$ can be obtained

$$E^\circ_{\text{red,sum}} = \frac{\Delta G^\circ_{\text{Rxn,sum}}}{-n_{\text{Rxn,sum}}F} = \frac{-331{,}800\ \text{J/mol}}{-(2\ \text{eq/mol})\,(96{,}500\ \text{C/eq})} \times \frac{1\ \text{V}}{1\ \text{J/C}}$$

$$= 1.72\ \text{V}$$

The E_H can be determined from the equation

$$E_H = E^\circ - \frac{0.059}{2}\log\left(\frac{[\text{Cl}^-]}{[\text{OCl}^-][\text{H}^+]^2}\right)$$

At the boundary, $[\text{Cl}^-]$ equals [HOCl] and the following expression may be obtained:

(4)

$$E_H = 1.72 - 0.059\ \text{pH}$$

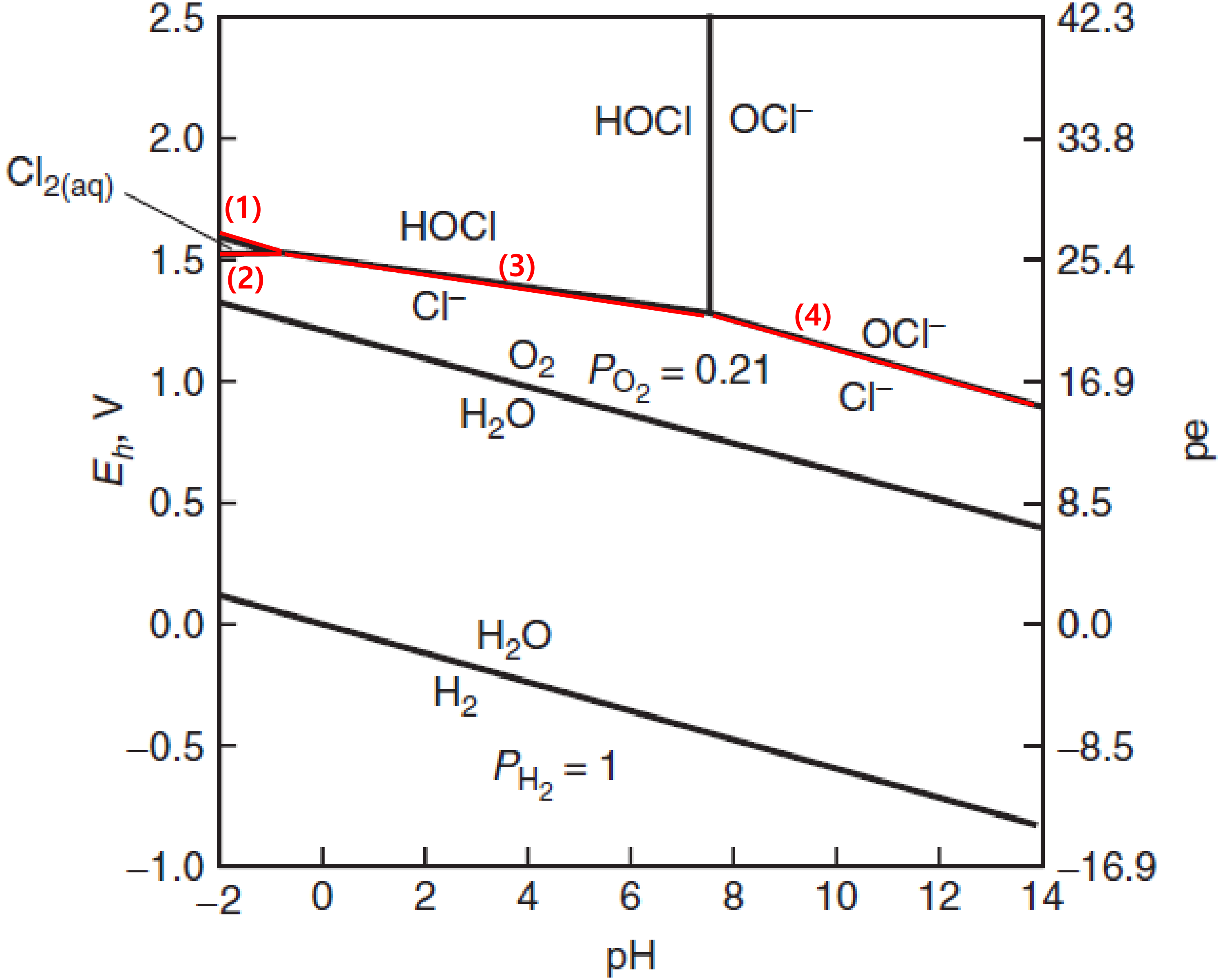


Figure
Predominance area diagram for chlorine system with total chlorine species concentration $C_{T,Cl}$ of 10^{-4} mol/L ($C_{T,Cl} = 10^{-4}$ mol/L $= 2[Cl_2(aq)] + [HOCl] + [OCl^-] + [Cl^-]$).

*pe = $-\log[e^-] = F/(2.3RT)E_h$

Kinetics of Redox Reactions

Rate of Oxidation–Reduction Processes

The reaction between an organic compound R (reductant) and an oxidant proceeds as shown in the following elementary reaction; and, based on numerous laboratory and full-scale studies, it has been found that second-order rate constants may be used to assess the rate of reaction:

$$\mathrm{R} + \text{oxidant}\ \left(\text{electron acceptor, } \mathrm{O_2}, \mathrm{O_3}, \mathrm{HO\bullet}\right)$$

$$\rightarrow \text{intermediate by-products}$$

$$\text{intermediate by-products} + \text{oxidant}$$

$$\rightarrow \mathrm{CO_2} + \mathrm{H_2O} + \text{mineral acids} \left(\text{e.g., HCl}\right)$$

$$r_R = -k_{ox} C_{ox} C_R$$

where r_R = rate of disappearance of organic compound R, mol/L · s
k_{ox} = second-order rate constant for oxidation reaction, L · mol/s
C_{ox} = concentration of oxidant, mol/L
C_R = concentration of organic compound R, mol/L

Homework

What would the E_h-pH diagram for chlorine species look like when the total chlorine concentration changes?

Think about it !

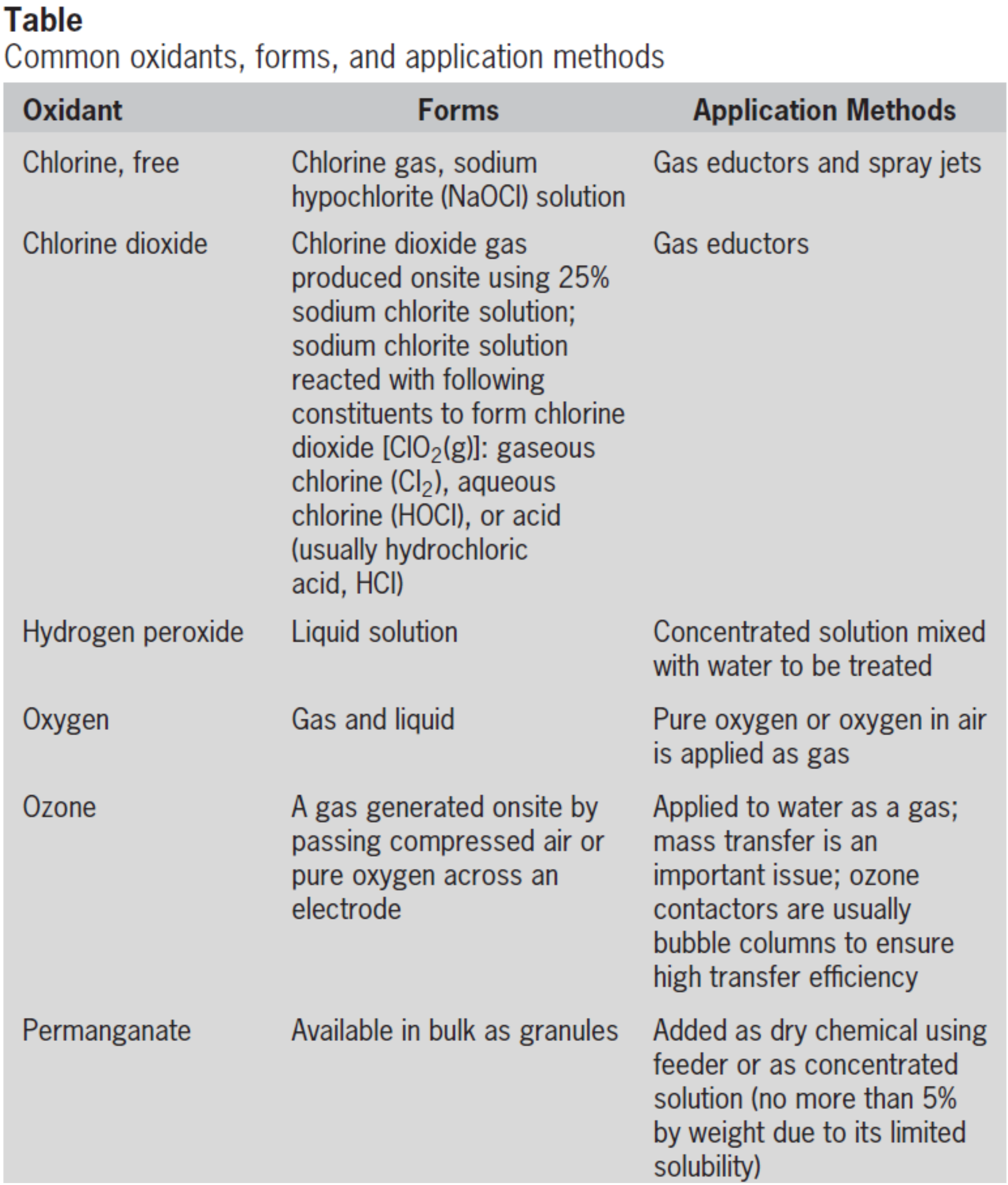
Common Chemical Oxidants for Water Treatment Applications

✓ Oxidation rate

$$HO\bullet > O_3 > H_2O_2$$

$$> HOCl > ClO_2 > KMnO_4$$

$$> Cl_2 > O_2$$



Table

Common oxidants, forms, and application methods

Oxidant	Forms	Application Methods
Chlorine, free	Chlorine gas, sodium hypochlorite (NaOCl) solution	Gas eductors and spray jets
Chlorine dioxide	Chlorine dioxide gas produced onsite using 25% sodium chlorite solution; sodium chlorite solution reacted with following constituents to form chlorine dioxide [ClO_2(g)]: gaseous chlorine (Cl_2), aqueous chlorine (HOCl), or acid (usually hydrochloric acid, HCl)	Gas eductors
Hydrogen peroxide	Liquid solution	Concentrated solution mixed with water to be treated
Oxygen	Gas and liquid	Pure oxygen or oxygen in air is applied as gas
Ozone	A gas generated onsite by passing compressed air or pure oxygen across an electrode	Applied to water as a gas; mass transfer is an important issue; ozone contactors are usually bubble columns to ensure high transfer efficiency
Permanganate	Available in bulk as granules	Added as dry chemical using feeder or as concentrated solution (no more than 5% by weight due to its limited solubility)

Oxygen (O_2)

- ✓ Redox potential

$$O_2(aq) + 4H^+ + 4e^- \rightarrow 2H_2O \qquad E^\circ_{red} = 1.27\ \mathrm{V}$$

- ✓ Applications
  - Oxidation of iron, manganese, and sulfides

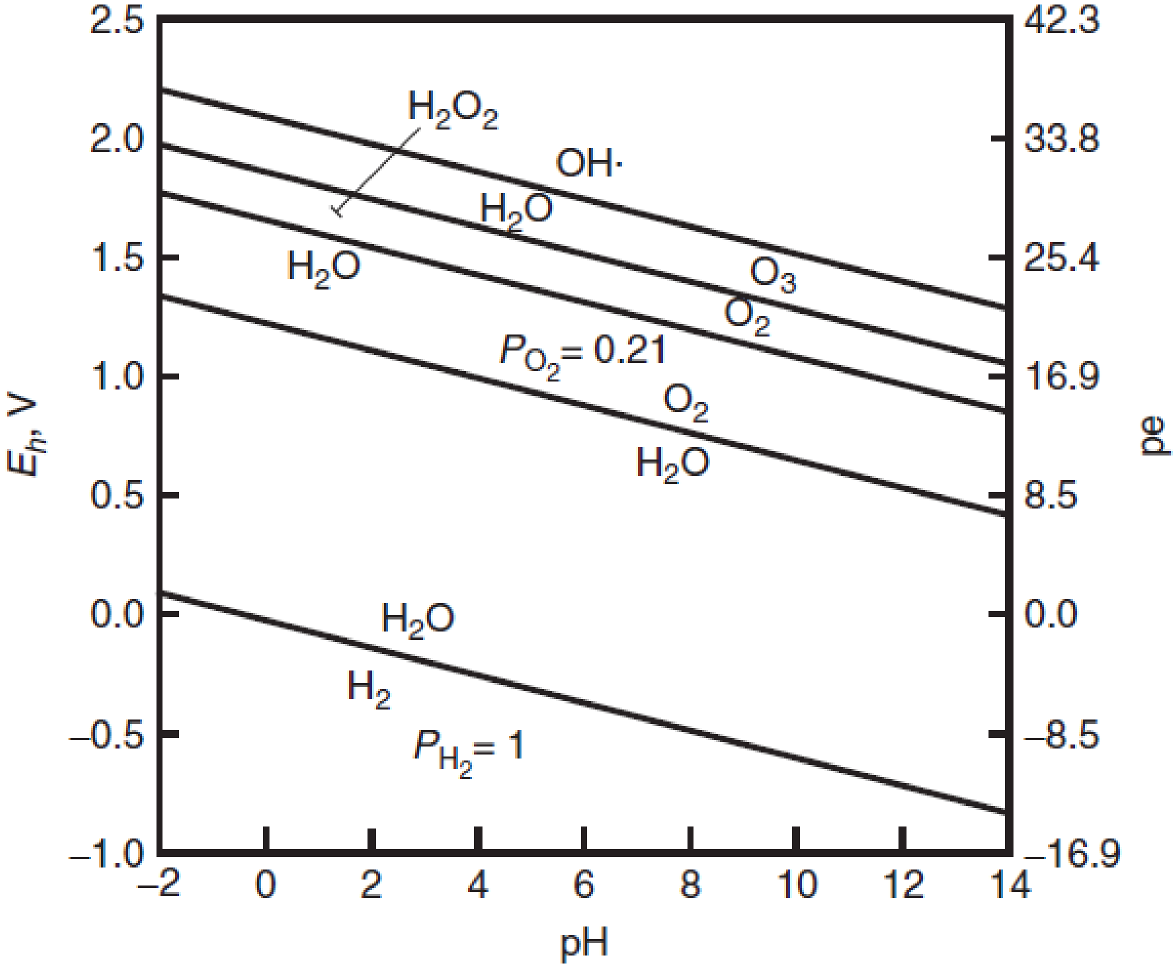


Figure
Predominance area diagram for oxygen system for oxygen concentration of 0.21 atm.

Chlorine (Cl_2)

✓ Redox potential

$$Cl_2(aq) + 2e^- \rightleftarrows 2Cl^- \qquad E^\circ_{\mathrm{red}} = 1.396\ \mathrm{V}$$

$$2HOCl + 2H^+ + 2e^- \rightleftarrows Cl_2(aq) + 2H_2O \qquad E^\circ_{\mathrm{red}} = 1.61\ \mathrm{V}$$

$$HOCl + H^+ + 2e^- \rightleftarrows Cl^- + H_2O \qquad E^\circ_{\mathrm{red}} = 1.50\ \mathrm{V}$$

$$OCl^- + H_2O + 2e^- \rightleftarrows Cl^- + 2OH^- \qquad E^\circ_{\mathrm{red}} = 0.90\ \mathrm{V}$$

✓ Applications

- Oxidation of iron, manganese, sulfides, taste and odor compounds (but not applicable to Geosmin & 2-MIB), ammonia

- Oxidation byproducts (chlorinated organic compounds) are problematic

Chlorine Dioxide (ClO_2)

✓ Redox potential

$$ClO_2\,(g) + 2H_2O + 5e^- \rightarrow Cl^- + 4OH^- E^{\circ}_{red} = 0.799\ V$$

$$ClO_2 + e^- \rightarrow ClO_2^- \quad E^{o}_{red} = 0.95{\sim}1\ V$$

✓ Decomposition

$$2ClO_2 + 2OH^- \rightarrow ClO_2^- + ClO_3^- + H_2O$$

✓ Applications

- Oxidation of iron, manganese, sulfides, taste and odor compounds (little applicable to Geosmin & 2-MIB), and some of organic compounds

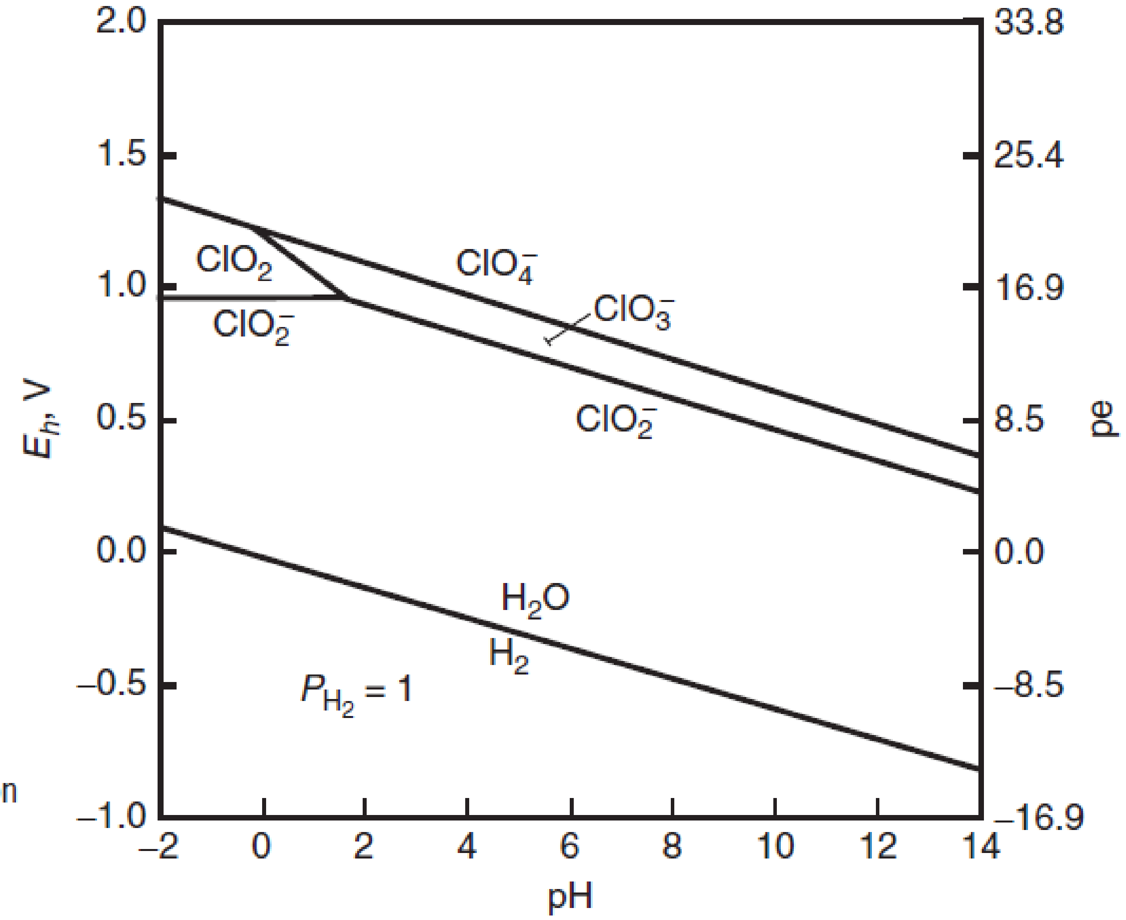


Figure
Predominance area diagram for chlorine dioxide system for total species concentration of 10^{-4} mol/L.

Hydrogen Peroxide (H_2O_2)

✓ Redox potential

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \qquad E^\circ_{\text{red}} = 1.780 \text{ V}$$

✓ Applications

- Oxidation of iron, sulfides
- A Reagent for advanced oxidation technology (a precursor of OH radical)
  e.g., UV/H_2O_2, O_3/H_2O_2, Fe(II)/H_2O_2

Ozone (O_3)

✓ Redox potential

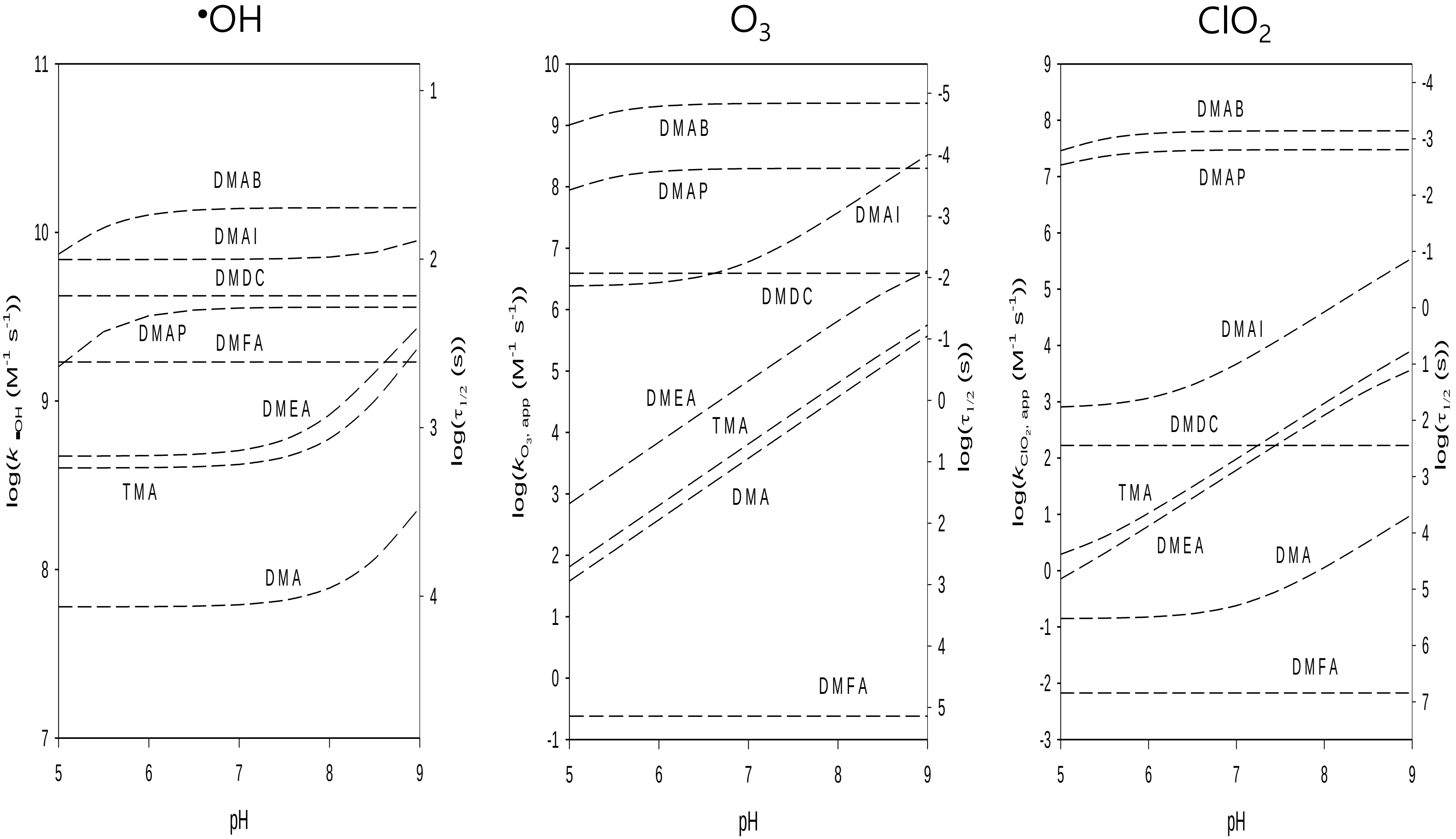
$$O_3\,(g) + 2H^+ + 2e^- \rightarrow O_2 + H_2O \qquad E^\circ_{\mathrm{red}} = 2.08\ \mathrm{V}$$

✓ Applications

- Oxidation of iron, manganese, sulfides, taste and odor compounds, micropollutamnts, removal of color, control of DBP precursors (oxidation of NOM)

- A Reagent for advanced oxidation technology (a precursor of OH radical)
  e.g., UV/O_3, O_3/H_2O_2, $Fe(II)/O_3$

✓ Second-order rate constants for reactions of NDMA precursors with oxidants



Source: Lee et al., 2007 (*Environ. Sci. Technol.*)

Permanganate (MnO_4^-)

✓ Redox potential

$$MnO_4^- + 4H^+ + 3e^- \rightleftarrows MnO_2\,(s) + 2H_2O \qquad E^\circ_{red} = 1.68\ V$$

$$MnO_4^- + 8H^+ + 5e^- \rightleftarrows Mn^{2+} + 4H_2O \qquad E^\circ_{red} = 1.510\ V$$

Under alkaline conditions the corresponding reduction half reaction is

$$MnO_4^- + 2H_2O + 3e^- \rightleftarrows MnO_2\,(s) + 4OH^- \qquad E^\circ_{red} = 0.590\ V$$

✓ Applications

- Oxidation of iron, manganese, taste and odor compounds
- Pink color: needs dosage control

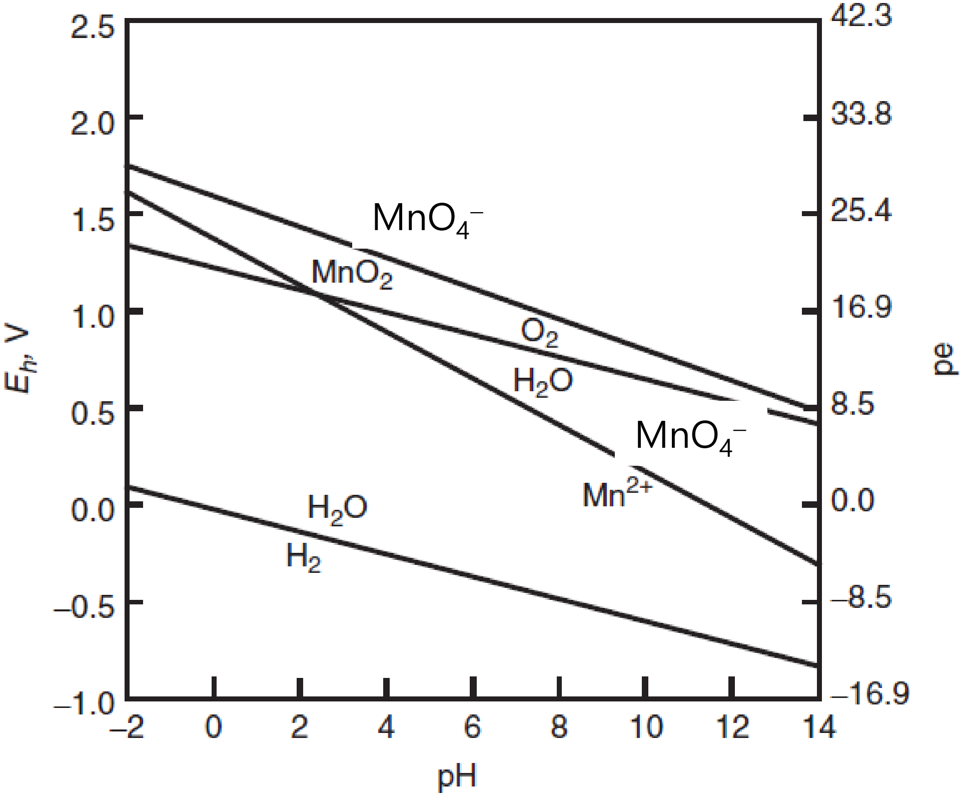


Figure
Predominance area diagram for permanganate system for total species concentration of 10^{-4} mol/L.