8 Chemical Oxidation and Reduction

Chapter 8 in
Bruce E. Crittenden, John C. et al.,
MWH's Water Treatment Principles
and Design (3rd Edition),
John Wiley & Sons, 2012

All the figures and tables in this material are from the above reference unless specified otherwise.

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., $O_2 + H_2 \rightarrow H_2O_2$

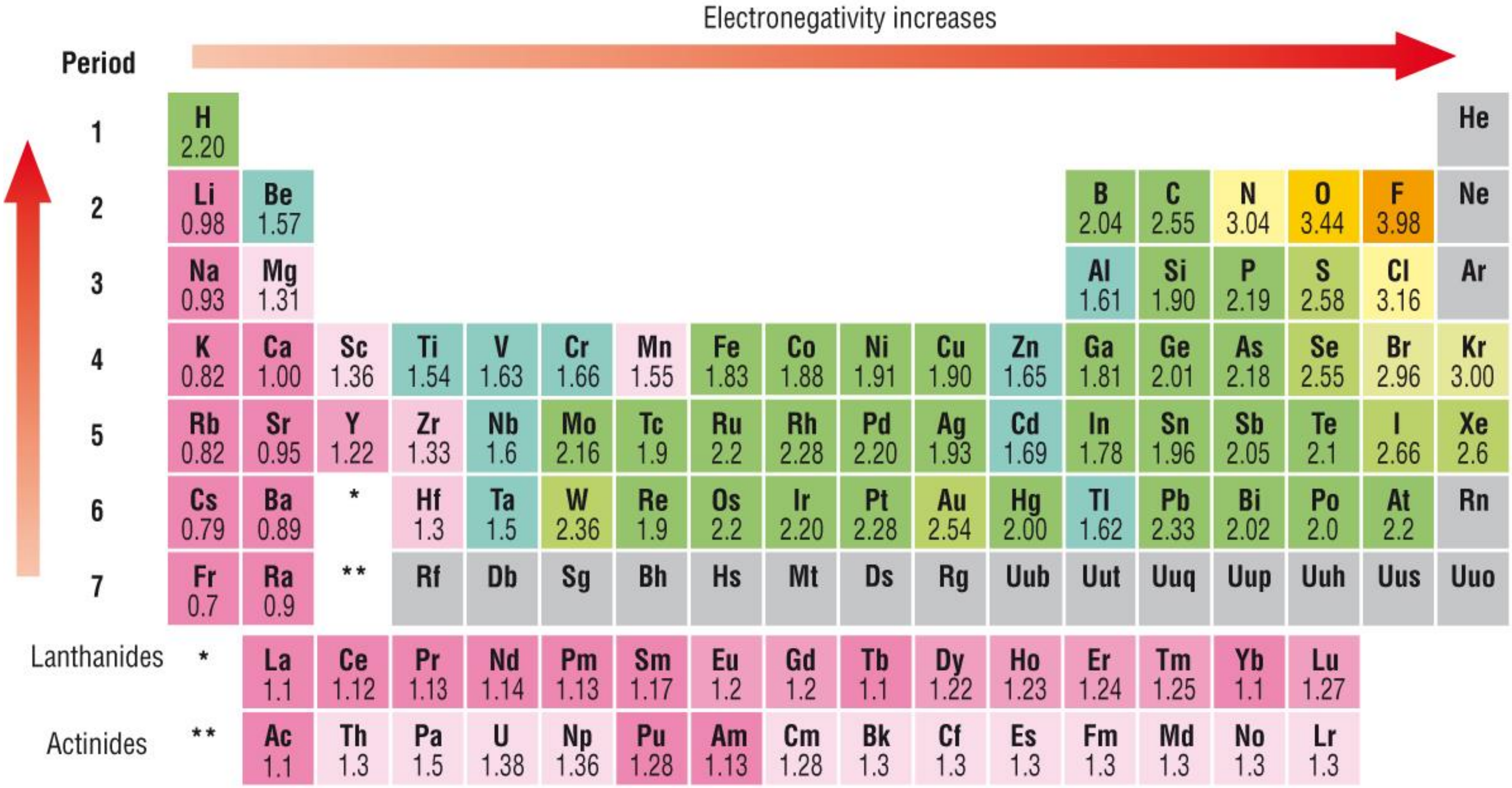
$O_2 + 2e^- + 2H^+ \rightarrow H_2O_2$

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

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

Oxidation number

How about this?



Electronegativity increases

Period																		
1	H 2.20																	He
2	Li 0.98	Be 1.57											B 2.04	C 2.55	N 3.04	O 3.44	F 3.98	Ne
3	Na 0.93	Mg 1.31											Al 1.61	Si 1.90	P 2.19	S 2.58	Cl 3.16	Ar
4	K 0.82	Ca 1.00	Sc 1.36	Ti 1.54	V 1.63	Cr 1.66	Mn 1.55	Fe 1.83	Co 1.88	Ni 1.91	Cu 1.90	Zn 1.65	Ga 1.81	Ge 2.01	As 2.18	Se 2.55	Br 2.96	Kr 3.00
5	Rb 0.82	Sr 0.95	Y 1.22	Zr 1.33	Nb 1.6	Mo 2.16	Tc 1.9	Ru 2.2	Rh 2.28	Pd 2.20	Ag 1.93	Cd 1.69	In 1.78	Sn 1.96	Sb 2.05	Te 2.1	I 2.66	Xe 2.6
6	Cs 0.79	Ba 0.89	*	Hf 1.3	Ta 1.5	W 2.36	Re 1.9	Os 2.2	Ir 2.20	Pt 2.28	Au 2.54	Hg 2.00	Tl 1.62	Pb 2.33	Bi 2.02	Po 2.0	At 2.2	Rn
7	Fr 0.7	Ra 0.9	**	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub	Uut	Uuq	Uup	Uuh	Uus	Uuo
Lanthanides	*	La 1.1	Ce 1.12	Pr 1.13	Nd 1.14	Pm 1.13	Sm 1.17	Eu 1.2	Gd 1.2	Tb 1.1	Dy 1.22	Ho 1.23	Er 1.24	Tm 1.25	Yb 1.1	Lu 1.27		
Actinides	**	Ac 1.1	Th 1.3	Pa 1.5	U 1.38	Np 1.36	Pu 1.28	Am 1.13	Cm 1.28	Bk 1.3	Cf 1.3	Es 1.3	Fm 1.3	Md 1.3	No 1.3	Lr 1.3		

Terminology for Chemical Oxidation and Reduction

Term	Definition
Advanced oxidation processes	Processes that generate hydroxyl radical at room temperature and pressure.
Anode	Electrode in a electrochemical cell where oxidation takes place.
Cathode	Electrode in a electrochemical cell where reduction takes place.
Chromophores	Functional groups or bonds on chemical compounds responsible for the absorption of light.
Conventional oxidation processes	Oxidation processes that achieve oxidation without the generation of hydroxyl radicals,
Electron acceptor	Reactant that gains electrons in a redox reaction; an oxidant.
Electron donor	Reactant that loses electrons in a redox reaction; a reductant.
Oxidant	Reactant that causes the oxidation of a reduced species in a redox reaction. Oxidants are electron acceptors.
Oxidation reaction	Chemical half-reaction in which a reactant loses electrons.
Reductant	Reactant that causes the reduction of an oxidized species in a redox reaction. Reductants are electron donors.
Redox reaction	Abbreviated name for oxidation–reduction reaction
Reduction reaction	Chemical half-reaction in which a reactant gains electrons.

8-1 Introduction to Use of Oxidation Processes in 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 8-1
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 (discussed in Chap. 13)

[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

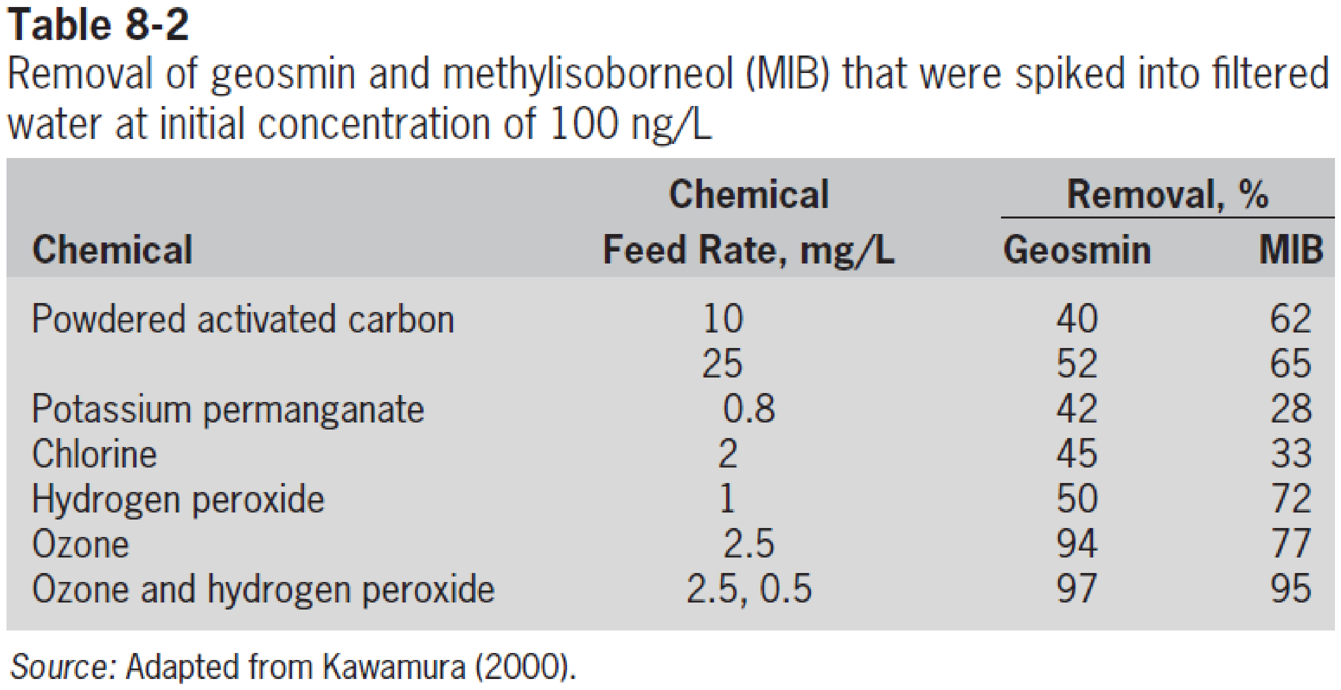


Table 8-2
Removal of geosmin and methylisoborneol (MIB) that were spiked into filtered water at initial concentration of 100 ng/L

	Chemical	Removal, %	
Chemical	**Feed Rate, mg/L**	**Geosmin**	**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

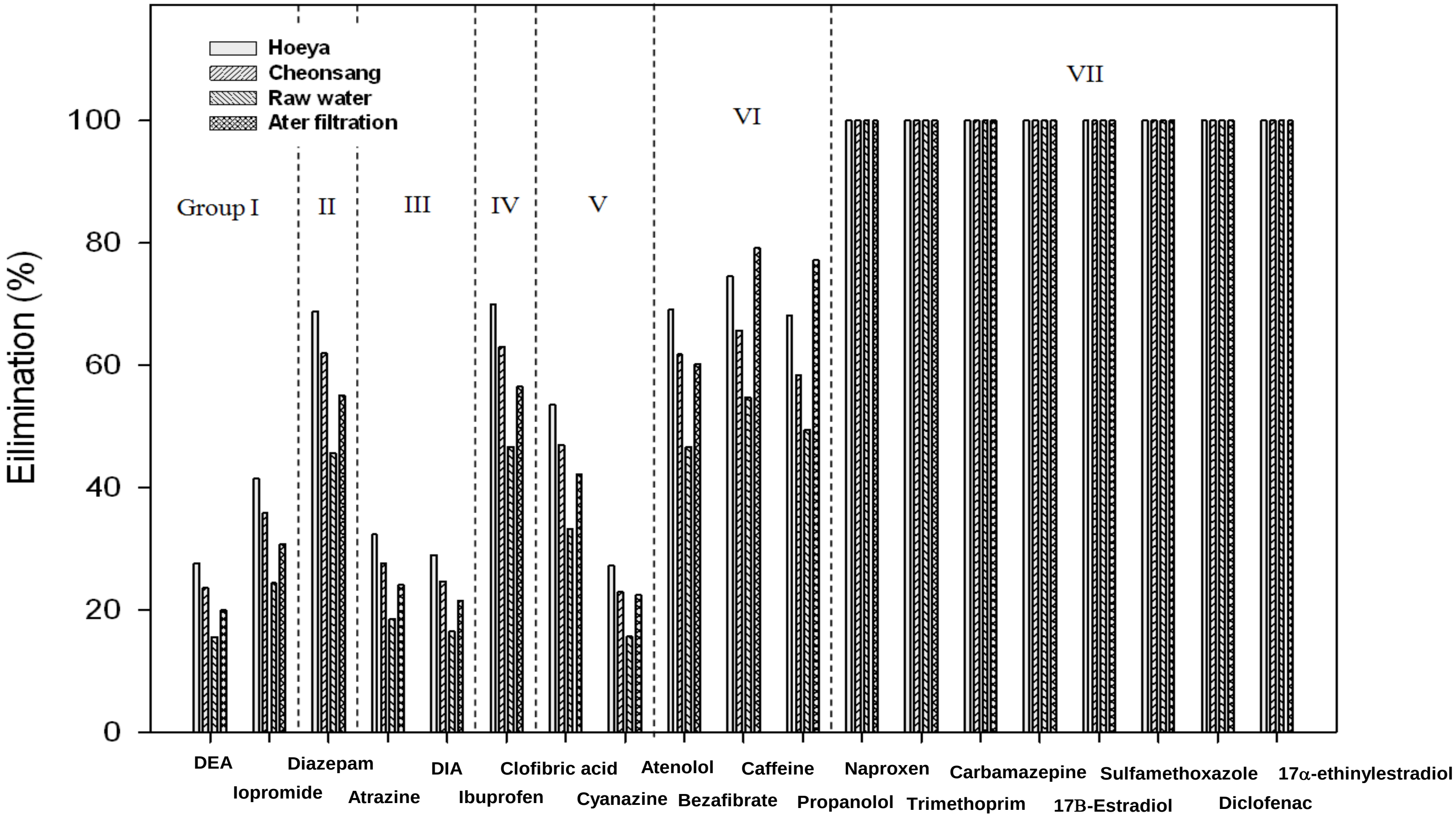
Source: Adapted from Kawamura (2000).

✓ **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

8-2 Fundamentals of Chemical Oxidation and Reduction

Introduction to Redox Reactions

- ✓ **Definitions of oxidation and reduction**
- ✓ **Half Reactions**

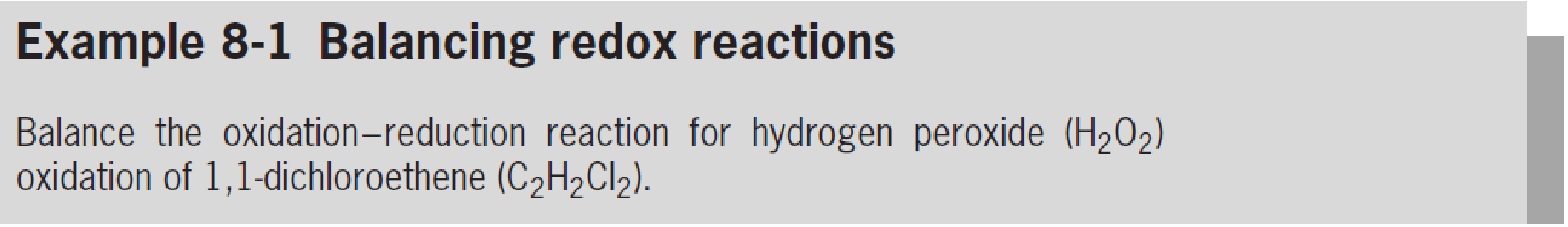
$$Mn^{2+} + O_3(aq) + H_2O \rightarrow MnO_2(s) + O_2(aq) + 2H^+ \qquad (8\text{-}1)$$

⬇

$$Mn^{2+} + 2H_2O \rightarrow MnO_2(s) + 4H^+ + 2e^- \qquad \text{(oxidation)} \qquad (8\text{-}2)$$

$$O_3(aq) + 2H^+ + 2e^- \rightarrow O_2(aq) + H_2O \qquad \text{(reduction)} \qquad (8\text{-}3)$$

- ✓ **Balancing Redox Reactions**



Example 8-1 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 Electrode Potentials and Redox Equilibrium Reactions

✓ MECHANISTIC DESCRIPTION OF ELECTRODE POTENTIALS WITH AN ELECTROCHEMICAL CELL

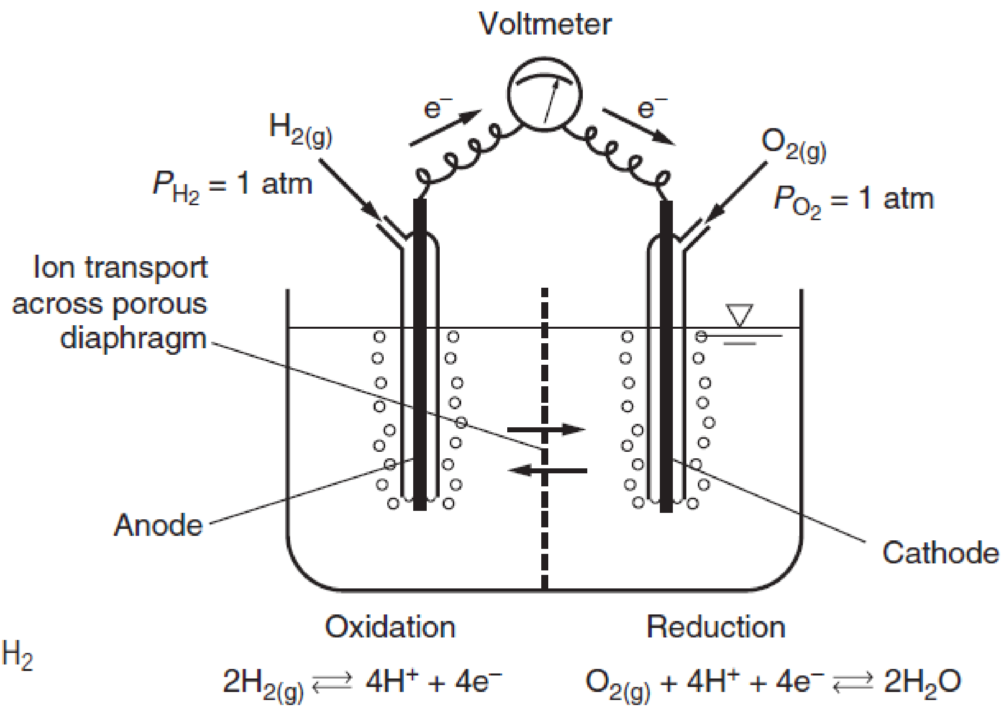


Figure 8-1
Cell potential for reaction between H_2 and O_2.

$$O_2\,(aq) + 4H^+ + 4e^- \rightleftarrows 2H_2O \qquad \text{(reduction)} \qquad E^\circ_{\text{red}} = 1.27\text{ V} \qquad (8\text{-}4)$$

$$H_2 \rightleftarrows 2H^+ + 2e^- \qquad \text{(oxidation)} \qquad E^\circ_{\text{ox}} = 0\text{ V} \qquad (8\text{-}5)$$

$$O_2 + 2H_2 \rightleftarrows 2H_2O \qquad \text{(overall)} \qquad E^\circ_{\text{Rxn}} = \;? \qquad (8\text{-}6)$$

$$E^\circ_{\text{Rxn}} = E^\circ_{\text{red}} + E^\circ_{\text{ox}}$$

$$= 1.27 + 0 = 1.27\text{V} \qquad (8\text{-}7)$$

✓ ASSESSING REACTION FEASIBILITY

$$\mathrm{MnO_2\,(s) + 4H^+ + 2e^- \rightleftarrows Mn^{2+} + 2H_2O} \quad \text{(reduction)} \quad E^\circ_{\mathrm{red}} = +1.230\ \mathrm{V} \quad (8\text{-}8)$$

$$\mathrm{H_2 \rightleftarrows 2H^+ + 2e^-} \quad \text{(oxidation)} \quad E^\circ_{\mathrm{ox}} = 0\ \mathrm{V} \quad (8\text{-}9)$$

$$\mathrm{MnO_2\,(s) + H_2 + 2H^+ \rightleftarrows Mn^{2+} + 2H_2O} \quad \text{(overall)} \quad E^\circ_{\mathrm{Rxn}} = +1.230\ \mathrm{V} \quad (8\text{-}10)$$

$$\mathrm{O_3\,(aq) + 2H^+ + 2e^- \rightleftarrows O_2\,(aq) + H_2O} \quad \text{(reduction)} \quad E^\circ_{\mathrm{red}} = +2.08\ \mathrm{V} \quad (8\text{-}11)$$

$$\mathrm{H_2 \rightleftarrows 2H^+ + 2e^-} \quad \text{(oxidation)} \quad E^\circ_{\mathrm{ox}} = 0\ \mathrm{V} \quad (8\text{-}12)$$

$$\mathrm{O_3\,(aq) + H_2 \rightleftarrows O_2 + H_2O} \quad \text{(overall)} \quad E^\circ_{\mathrm{Rxn}} = +2.08\ \mathrm{V} \quad (8\text{-}13)$$

$E^\circ_{\mathrm{Rxn}} > 0$ Thermodynamically favored

E°_{Red} values are usually available from the literature databases !

$$\mathrm{A} + \frac{b}{a}\mathrm{B} \rightarrow \frac{c}{a}\mathrm{C} + \frac{d}{a}\mathrm{D} \tag{8-14}$$

$$\Delta G_{\mathrm{Rxn}} = \Delta G^{\circ}_{\mathrm{Rxn}} + RT \ln\left(\frac{\{\mathrm{C}\}^{c/a}\{\mathrm{D}\}^{d/a}}{\{\mathrm{A}\}\{\mathrm{B}\}^{b/a}}\right) \tag{8-15}$$

$$E_{\mathrm{Rxn}} = \frac{\Delta G_{\mathrm{Rxn}}}{-nF} \tag{8-16}$$

$$E_{\mathrm{Rxn}} = E^{\circ}_{\mathrm{Rxn}} - \frac{RT}{nF}\ln\left(\frac{\{\mathrm{C}\}^{c/a}\{\mathrm{D}\}^{d/a}}{\{\mathrm{A}\}\{\mathrm{B}\}^{b/a}}\right)$$

$$\text{or} \quad E^{\circ}_{\mathrm{Rxn}} - \frac{2.303RT}{nF}\log\left(\frac{\{\mathrm{C}\}^{c/a}\{\mathrm{D}\}^{d/a}}{\{\mathrm{A}\}\{\mathrm{B}\}^{b/a}}\right) \tag{8-17}$$

where ΔG_{Rxn} = free-energy change of reaction, J/mol

$\Delta G^{\circ}_{\mathrm{Rxn}}$ = free-energy change of reaction under standard conditions, J/mol

E_{Rxn} = electrode potential of reaction = $E_{\mathrm{ox}} + E_{\mathrm{red}}$, V

E°_{Rxn} = standard electrode potential of reaction, V

n = number of electrons transferred in reaction, eq/mol

F = Faraday's constant, 96,500 C/eq

R = universal gas constant, 8.314 J/mol · K

T = absolute temperature, K

$\{i\}$ = activity of constituent i (A, B, C, or D), mol/L

$$\Delta G^\circ_{\mathrm{Rxn}} = -n_{\mathrm{Rxn}} F E^\circ_{\mathrm{Rxn}} = \Delta G^\circ_{\mathrm{ox}} + \Delta G^\circ_{\mathrm{red}} = -n_{\mathrm{ox}} F E^\circ_{\mathrm{ox}} - n_{\mathrm{red}} F E^\circ_{\mathrm{red}} \qquad (8\text{-}18)$$

where n_{Rxn} = number of electrons transferred in overall reaction, eq/mol

E°_{Rxn} = standard electrode potential of redox reaction, V

$\Delta G^\circ_{\mathrm{ox}}$ = standard free-energy change of oxidation half reaction, J/mol

$\Delta G^\circ_{\mathrm{red}}$ = standard free-energy change of reduction half reaction, J/mol

E°_{ox} = standard electrode potential of oxidation half reaction, V

E°_{red} = standard electrode potential of reduction half reaction, V

n_{ox} = number of electrons produced in oxidation half reaction, eq/mol

n_{red} = number of electrons obtained in reduction half reaction, eq/mol

Example 8-2 Oxidation power of oxygen and hydrogen peroxide

Investigate whether oxygen (O_2) or hydrogen peroxide (H_2O_2) is the more powerful oxidant from a consideration of free energy.

Solution

1. Write the reduction and oxidation half reactions of H_2O_2 as well as the overall reaction. From Table E1 at the website listed in App. E, the half reaction of H_2O_2 can be written with respect to the hydrogen electrode as follows:

$$\begin{array}{rll} H_2O_2 + 2H^+ + 2e^- \rightleftarrows 2H_2O & \text{(reduction)} & E^\circ_{\text{red}} = 1.780\ \text{V} \\ H_2 \rightleftarrows 2H^+ + 2e^- & \text{(oxidation)} & E^\circ_{\text{ox}} = 0\ \text{V} \\ \hline H_2O_2 + H_2 \rightleftarrows 2H_2O & \text{(overall)} & E^\circ_{\text{Rxn, }H_2O_2} = 1.780\ \text{V} \end{array}$$

2. Calculate $\Delta G^\circ_{\text{Rxn, }H_2O_2}$ using Eq. 8-18 (note J/C = V):

$$\Delta G^\circ_{\text{Rxn, }H_2O_2} = -nFE^\circ_{\text{Rxn, }H_2O_2} = -\,(2\ \text{eq/mol})\,(96{,}500\ \text{C/eq})\,(1.780\ \text{J/C})$$

$$= -343{,}540\ \text{J/mol} \quad (-343.5\ \text{kJ/mol})$$

3. Write the reduction and oxidation half reactions of O_2 as well as the overall reaction: The half reaction of O_2 can be written with respect to the hydrogen electrode as follows:

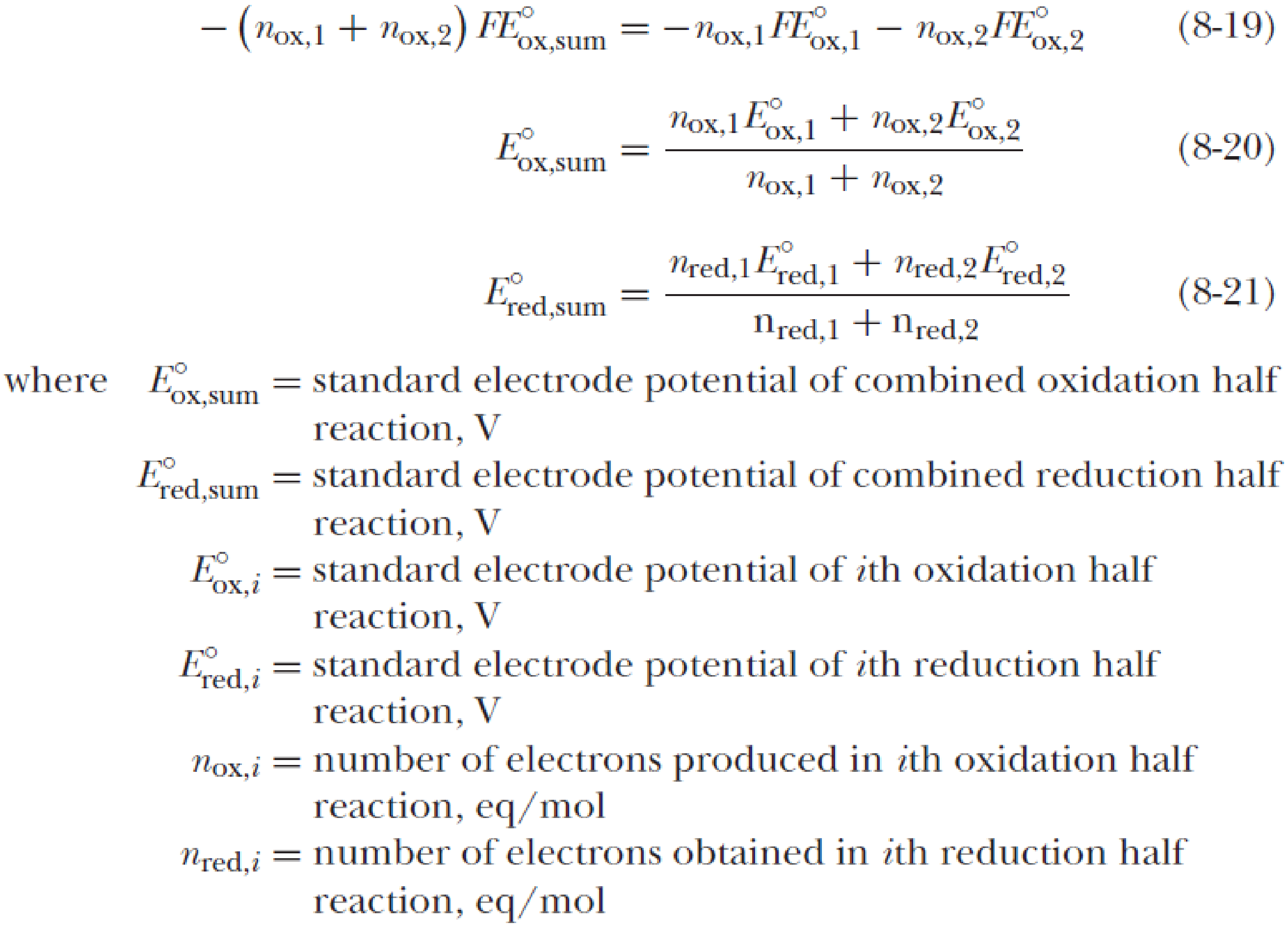
$$\begin{array}{rll} O_2\,(aq) + 4H^+ + 4e^- \rightleftarrows 2H_2O & \text{(reduction)} & E^\circ_{\text{red}} = 1.27\ \text{V} \\ 2(H_2 \rightleftarrows 2H^+ + 2e^-) & \text{(oxidation)} & E^\circ_{\text{ox}} = 0\ \text{V} \\ \hline O_2 + 2H_2 \rightleftarrows 2H_2O & \text{(overall)} & E^\circ_{\text{Rxn},O_2} = 1.27\ \text{V} \end{array}$$

4. Calculate $\Delta G^\circ_{\text{Rxn},O_2}$ by rearranging Eq. 8-18:

$$\Delta G^\circ_{\text{Rxn},O_2} = -nFE^\circ_{\text{Rxn},O_2} = -\,(4\ \text{eq/mol})\,(96{,}500\ \text{C/eq})\,(1.27\ \text{J/C})$$

$$= -490{,}220\ \text{J/mol} \quad (-490\ \text{kJ/mol})$$

- Potential of combined reactions



$$-\left(n_{\text{ox},1}+n_{\text{ox},2}\right)FE^{\circ}_{\text{ox,sum}}=-n_{\text{ox},1}FE^{\circ}_{\text{ox},1}-n_{\text{ox},2}FE^{\circ}_{\text{ox},2} \tag{8-19}$$

$$E^{\circ}_{\text{ox,sum}}=\frac{n_{\text{ox},1}E^{\circ}_{\text{ox},1}+n_{\text{ox},2}E^{\circ}_{\text{ox},2}}{n_{\text{ox},1}+n_{\text{ox},2}} \tag{8-20}$$

$$E^{\circ}_{\text{red,sum}}=\frac{n_{\text{red},1}E^{\circ}_{\text{red},1}+n_{\text{red},2}E^{\circ}_{\text{red},2}}{\mathrm{n}_{\text{red},1}+\mathrm{n}_{\text{red},2}} \tag{8-21}$$

where $E^{\circ}_{\text{ox,sum}}$ = standard electrode potential of combined oxidation half reaction, V

$E^{\circ}_{\text{red,sum}}$ = standard electrode potential of combined reduction half reaction, V

$E^{\circ}_{\text{ox},i}$ = standard electrode potential of *i*th oxidation half reaction, V

$E^{\circ}_{\text{red},i}$ = standard electrode potential of *i*th reduction half reaction, V

$n_{\text{ox},i}$ = number of electrons produced in *i*th oxidation half reaction, eq/mol

$n_{\text{red},i}$ = number of electrons obtained in *i*th reduction half reaction, eq/mol

Example 8-3 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:

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

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

$$E^\circ_{ox,sum} = \frac{2\,(-1.33\text{ V}) + 4\,(1.49\text{ V})}{2 + 4} = -1.437\text{ V}$$

- Determining equilibrium constant from electrical potential

$$0 = E^{\circ}_{\text{Rxn}} - \frac{RT}{nF} \ln K_{\text{eq}} \qquad (8\text{-}22)$$

$$K_{\text{eq}} = e^{nFE^{\circ}_{\text{Rxn}}/RT} = e^{-\Delta G^{\circ}_{\text{Rxn}}/RT} \qquad (8\text{-}23)$$

Example 8-4 Oxidation of Fe(s) with dissolved oxygen

Calculate the equilibrium constant and $\Delta G^{\circ}_{\text{Rxn}}$ for the corrosion of Fe(s) to Fe^{2+} by dissolved oxygen. Determine the oxygen concentrations that are needed for pH values equal to 5.5, 7.0, and 8.5 such that the reaction is thermodynamically favorable. *Given:* $[Fe^{2+}] = 10^{-6}$ M and temperature is 298 K.

Solution

1. Write the reduction and oxidation half reactions for corrosion of Fe(s) to Fe^{2+} by reacting with oxygen as well as the overall reaction:
From Table E1 at the website listed in App. E, the corrosion of Fe(s) to Fe^{2+} by reacting with oxygen can be written as

$$2[\mathrm{Fe\,(s)} \rightleftarrows \mathrm{Fe}^{2+} + 2\mathrm{e}^-] \qquad \text{(oxidation)} \quad E^\circ_{\mathrm{ox}} = 0.44\ \mathrm{V}$$

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

$$2\mathrm{Fe\,(s)} + \mathrm{O_2\,(aq)} + 4\mathrm{H}^+ \rightleftarrows 2\mathrm{Fe}^{2+} + 2\mathrm{H_2O} \qquad \text{(overall)} \quad E^\circ_{\mathrm{Rxn}} = 1.71\ \mathrm{V}$$

2. Calculate the equilibrium constant K_{eq} using Eq. 8-23:

$$K_{eq} = \exp\left(\frac{nFE^\circ_{\mathrm{Rxn}}}{RT}\right) = \exp\left[\frac{(4\ \mathrm{eq/mol})\,(96{,}500\ \mathrm{C/eq})\,(1.71\ \mathrm{J/C})}{(8.314\ \mathrm{J/mol\cdot K})\,(298\ \mathrm{K})}\right]$$

$$= 4.97 \times 10^{115}$$

3. Determine the equilibrium oxygen concentrations at pH values equal to 5.5, 7.0, and 8.5 using the expression developed in step 1 $[2\mathrm{Fe(s)} + \mathrm{O_2(aq)} + 4\mathrm{H}^+ \rightleftarrows 2\mathrm{Fe}^{2+} + 2\mathrm{H_2O}]$ and the equilibrium value developed in step 2:

$$K_{eq} = \frac{\{\mathrm{Fe}^{2+}\}^2\{\mathrm{H_2O}\}^2}{\{\mathrm{Fe(s)}\}^2\{\mathrm{O_2(aq)}\}\{\mathrm{H}^+\}^4}$$

Neglecting activity coefficient corrections and assuming the activity of solids and liquids is equal to 1,

$$[\mathrm{O_2(aq)}] = \frac{[\mathrm{Fe}^{2+}]^2}{[\mathrm{H}^+]^4 K_{eq}} = \frac{(10^{-6})^2}{[\mathrm{H}^+]^4(4.97 \times 10^{115})}$$

Therefore,

$$[O_2\,(aq)] = \begin{cases} \dfrac{[\mathrm{Fe}^{2+}]^2}{[\mathrm{H}^+]^4 K_{eq}} = \dfrac{(10^{-6})^2}{(10^{-8.5})^4\,(4.97 \times 10^{115})} = 2.01 \times 10^{-94}\ \mathrm{M\ at\ pH\ 8.5} \\ \dfrac{[\mathrm{Fe}^{2+}]^2}{[\mathrm{H}^+]^4 K_{eq}} = \dfrac{(10^{-6})^2}{(10^{-7})^4\,(4.97 \times 10^{115})} = 2.01 \times 10^{-100}\ \mathrm{M\ at\ pH\ 7} \\ \dfrac{[\mathrm{Fe}^{2+}]^2}{[\mathrm{H}^+]^4 K_{eq}} = \dfrac{(10^{-6})^2}{(10^{-5.5})^4\,(4.97 \times 10^{115})} = 2.01 \times 10^{-106}\ \mathrm{M\ \ at\ pH\ 5.5} \end{cases}$$

Note: When the reaction quotient $Q = K_{eq}$, $\Delta G = 0$. If $\Delta G < 0$, the reaction is thermodynamically favorable. Thus, if the actual oxygen concentrations are greater than the equilibrium values computed above as a function of pH, the reaction will proceed as written in step 1.

- Impact of pH on reduction potential

??? + ne^- + $n` H^+$ → ???

E(pH) – E°(pH = 0) =

$$\begin{aligned}\Delta E^\circ_{\text{red}} &= -\left(\frac{2.303RT}{nF}\right)\log\left(\frac{1}{[\text{H}^+]^{n}}\right)\\ &= -\left[\frac{(2.303)\,(8.314\ \text{J/mol}\cdot\text{K})\,(298\ \text{K})}{(96{,}500\ \text{C/eq})\,(n\ \text{eq/mol})}\right]\text{pH}\\ &= -\left(\frac{0.0591}{n}\right) n` \times \text{pH} \qquad (8\text{-}24)\end{aligned}$$

where $\Delta E^\circ_{\text{red}}$ = change in potential, V

R = universal gas constant, 8.314 J/mol · K

T = absolute temperature, K

n = number of electrons transferred, eq/mol

F = Faraday's constant, 96,500 C/eq

$[\text{H}^+]$ = concentration of hydrogen ion, mol/L

pH = $\log([\text{H}^+]) = \log(1/[\text{H}^+])$, unitless

Example 8-5 Oxidation of manganese with ozone

Manganese [Mn(II)] is soluble in water and is present in many groundwaters because insoluble forms (e.g., MnO_2) that are contained in minerals are reduced to soluble forms. The subsurface is a reducing environment because electron acceptors such as oxygen have been used up by heterotrophic bacteria in the top organic-rich layer of soil. Ozone (O_3) is sometimes used to remove Mn^{2+}. Assume that the ozone and dissolved oxygen (DO) do not react with anything but Mn^{2+} (a simplifying assumption because ozone will react with many other constituents in a real water) and the pH is constant. Then:

1. Balance the overall redox reaction for the oxidation of Mn^{2+} to $MnO_2(s)$ with O_3.
2. Calculate the equilibrium constant.
3. Calculate the equilbrium Mn^{2+} concentration when the pH is 7, DO is 5 mg/L, and the ozone concentration is 0.5 mg/L.
4. Obtain expressions for DO, ozone, and $MnO_2(s)$ concentrations in terms of $Mn^{2+}(s)$ concentration. The initial reactant concentrations are [DO] $=$ 10 mg/L, ozone concentration $=$ 3 mg/L, and Mn^{2+} $=$ 2 mg/L and pH is 7.
5. Plot the free energy as a function of the conversion of Mn^{2+} from 0.01 to 0.999.

Use the stoichiometric table to determine all reacting species as a function of X_A and then eliminate X_A by using the final concentration C_A. After substituting C_A back into the expressions, DO, ozone, and MnO_2 concentrations can be obtained in terms of the final concentration of Mn^{2+}.

Solution

1. Balance the overall redox reaction:
   a. Identify the oxidation and reduction reactions and determine the standard electrode potential:

$$\text{Oxidation reaction:}\quad \mathrm{Mn^{2+} + 2H_2O \rightleftarrows MnO_2\,(s) + 4H^+ + 2e^-} \qquad E^\circ = -1.23\ \mathrm{V}$$

$$\text{Reduction reaction:}\quad \mathrm{O_3\,(aq) + 2H^+ + 2e^- \rightleftarrows O_2\,(aq) + H_2O} \qquad E^\circ = +2.08\ \mathrm{V}$$

   b. Balance the overall redox reaction by adding the two half reactions:

$$\begin{array}{lll}
\mathrm{Mn^{2+} + 2H_2O \rightleftarrows MnO_2\,(s) + 4H^+ + 2e^-} & \text{(oxidation)} & E^\circ_{\mathrm{ox}} = -1.23\ \mathrm{V} \\
\mathrm{O_3\,(aq) + 2H^+ + 2e^- \rightleftarrows O_2\,(aq) + H_2O} & \text{(reduction)} & E^\circ_{\mathrm{red}} = +2.08\ \mathrm{V} \\
\hline
\mathrm{Mn^{2+} + O_3\,(aq) + H_2O \rightleftarrows MnO_2\,(s) + O_2\,(aq) + 2H^+} & \text{(overall)} & E^\circ_{\mathrm{Rxn}} = 0.850\ \mathrm{V}
\end{array}$$

$$E^\circ_{\mathrm{Rxn}} = 2.08 + (-1.23) = 0.850\ \mathrm{V}$$

2. Calculate the equilibrium constant:
   a. Calculate $\Delta G^\circ_{\mathrm{Rxn}}$ using Eq. 8-16:

$$\Delta G^\circ_{\mathrm{Rxn}} = -nFE^\circ_{\mathrm{Rxn}} = -\,(2\ \mathrm{eq/mol})\,(96{,}500\ \mathrm{C/eq})\,(0.850\ \mathrm{J/C})$$

$$= -164{,}050\ \mathrm{J/mol} = -164.05\ \mathrm{kJ/mol}$$

   b. Calculate the equilibrium constant K_{eq} using Eq. 8-23:

$$K_{\mathrm{eq}} = e^{-\Delta G^\circ_{\mathrm{Rxn}}/RT} = e^{-(-164.05)/(8.314\times10^{-3}\times298)} = 5.71 \times 10^{28}$$

3. Calculate the equilibrium Mn^{2+} concentration when the pH is 7, DO is 5 mg/L, and the ozone concentration is 0.5 mg/L:

$$[H^+] = 10^{-7}\ M$$

$$[O_3(aq)] = 0.5\ mg/L = 1.04 \times 10^{-5}\ M$$

$$[O_2(aq)] = 5\ mg/L = 1.56 \times 10^{-4}\ M$$

$$K_{eq} = \frac{[O_2(aq)][H^+]^2}{[Mn^{2+}][O_3(aq)]}$$

$$[Mn^{2+}] = \frac{[O_2(aq)][H^+]^2}{K_{eq}[O_3(aq)]} = \frac{(1.56 \times 10^{-4})(10^{-7})^2}{(5.71 \times 10^{28})(1.04 \times 10^{-5})}$$

$$= 2.63 \times 10^{-42}\ M = 1.44 \times 10^{-37}\ mg/L$$

4. Obtain an expression for DO, ozone, and MnO_2 in terms of Mn^{2+}:
Initial concentrations:

$$[Mn^{2+}]_0 = 2\ mg/L = 3.64 \times 10^{-5}\ M$$

$$[O_3(aq)]_0 = 3\ mg/L = 6.25 \times 10^{-5}\ M$$

$$[O_2(aq)]_0 = 10\ mg/L = 3.13 \times 10^{-4}\ M$$

According to the overall reaction and Eqs. 8-29 to 8-31, the molar concentrations of $O_3(aq)$ and $O_2(aq)$ can be expressed in terms of $[Mn^{2+}]$ as

$$\begin{aligned}[O_3(aq)] &= [O_3(aq)]_0 - ([Mn^{2+}]_0 - [Mn^{2+}]) \\ &= 6.25 \times 10^{-5} - (3.64 \times 10^{-5} - [Mn^{2+}]) \\ &= 2.61 \times 10^{-5} + [Mn^{2+}]\end{aligned}$$

$$\begin{aligned}[O_2(aq)] &= [O_2(aq)]_0 + ([Mn^{2+}]_0 - [Mn^{2+}]) \\ &= 3.13 \times 10^{-4} + (3.64 \times 10^{-5} - [Mn^{2+}]) \\ &= 3.49 \times 10^{-4} - [Mn^{2+}]\end{aligned}$$

Because $MnO_2(s)$ is a solid in water, its activity is unity.

5. Plot the free energy as a function of the conversion of Mn^{2+} from 0.01 to 0.999:
   a. Obtain an expression of free energy as a function of the conversion of Mn^{2+}:
      Assume the conversion of Mn^{2+} is $X_{Mn^{2+}}$. According to the overall reaction and Eqs. 8-25 to 8-28, the molar concentrations of Mn^{2+}, H^+, $O_3(aq)$, and $O_2(aq)$ can be expressed as

$$[Mn^{2+}] = [Mn^{2+}]_0(1 - X_{Mn^{2+}})$$

$$= 3.64 \times 10^{-5}(1 - X_{Mn^{2+}})$$

$$[H^+] = [H^+]_0 + 2[Mn^{2+}]_0 X_{Mn^{2+}}$$

$$= 10^{-7} + 7.28 \times 10^{-5} X_{Mn^{2+}}$$

$$[O_3(aq)] = [O_3(aq)]_0 - [Mn^{2+}]_0 X_{Mn^{2+}}$$

$$= 6.25 \times 10^{-5} - 3.64 \times 10^{-5} X_{Mn^{2+}}$$

$$[O_2(aq)] = [O_2(aq)]_0 - [Mn^{2+}]_0 X_{Mn^{2+}}$$

$$= 3.13 \times 10^{-4} + 3.64 \times 10^{-5} X_{Mn^{2+}}$$

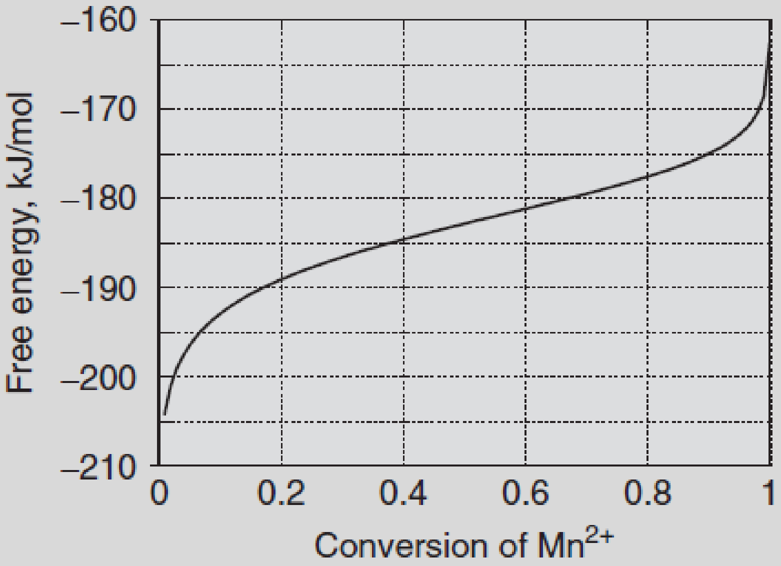
The free-energy expression (Eq. 8-15) can be written as given below by substituting the quotient Q for the logarithmic term in Eq. 8-15. The quotient is described in greater detail in Chap. 5.

$$\Delta G_{Rxn} = \Delta G^\circ_{Rxn} + RT\ln(Q) = \Delta G^\circ_{Rxn} + RT\ln\left(\frac{[O_2(aq)][H^+]^2}{[Mn^{2+}][O_3(aq)]}\right)$$

$$= -164.05 + (8.314 \times 10^{-3})(298)$$

$$\times \ln\left\{\frac{\left(3.13\times10^{-4} + 3.64\times10^{-5}X_{Mn^{2+}}\right)\left(10^{-7} + 7.28\times10^{-5}X_{Mn^{2+}}\right)^2}{\left[3.64\times10^{-5}\left(1 - X_{Mn^{2+}}\right)\right]\left(6.25\times10^{-5} - 3.64\times10^{-5}X_{Mn^{2+}}\right)}\right\}$$

b. Plot the free energy as a function of the conversion of Mn^{2+} from 0.01 to 0.999:



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

- ✓ **OXYGEN**

$$O_2(g) + 4H^+ + 4e^- \rightleftarrows 2H_2O \quad E^\circ_{red} = 1.23\ \text{V} \qquad (8\text{-}32)$$

$$E_H = E^\circ - \frac{0.059}{n}\log\frac{1}{[H^+]^4 P_{O_2}} \qquad (8\text{-}33)$$

$$= E^\circ - \frac{0.059}{4}(4\text{pH} - \log P_{O_2}) \qquad (8\text{-}34)$$

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

$$E_H = 1.24 - 0.059\text{pH} \qquad (8\text{-}35)$$

- ✓ **HYDROGEN**

$$2H_2O + 2e^- \rightleftarrows H_2(g) + 2OH^- E^\circ = -0.828\ \text{V} \qquad (8\text{-}36)$$

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

$$E_H = E^\circ - \frac{0.059}{2}(-2\text{pOH} + \log P_{H_2}) \qquad (8\text{-}37)$$

Assuming $P_{H_2} = 1$ atm, Eq. 8-37 results in the expression

$$E_H = -0.059\text{pH} \qquad (8\text{-}38)$$

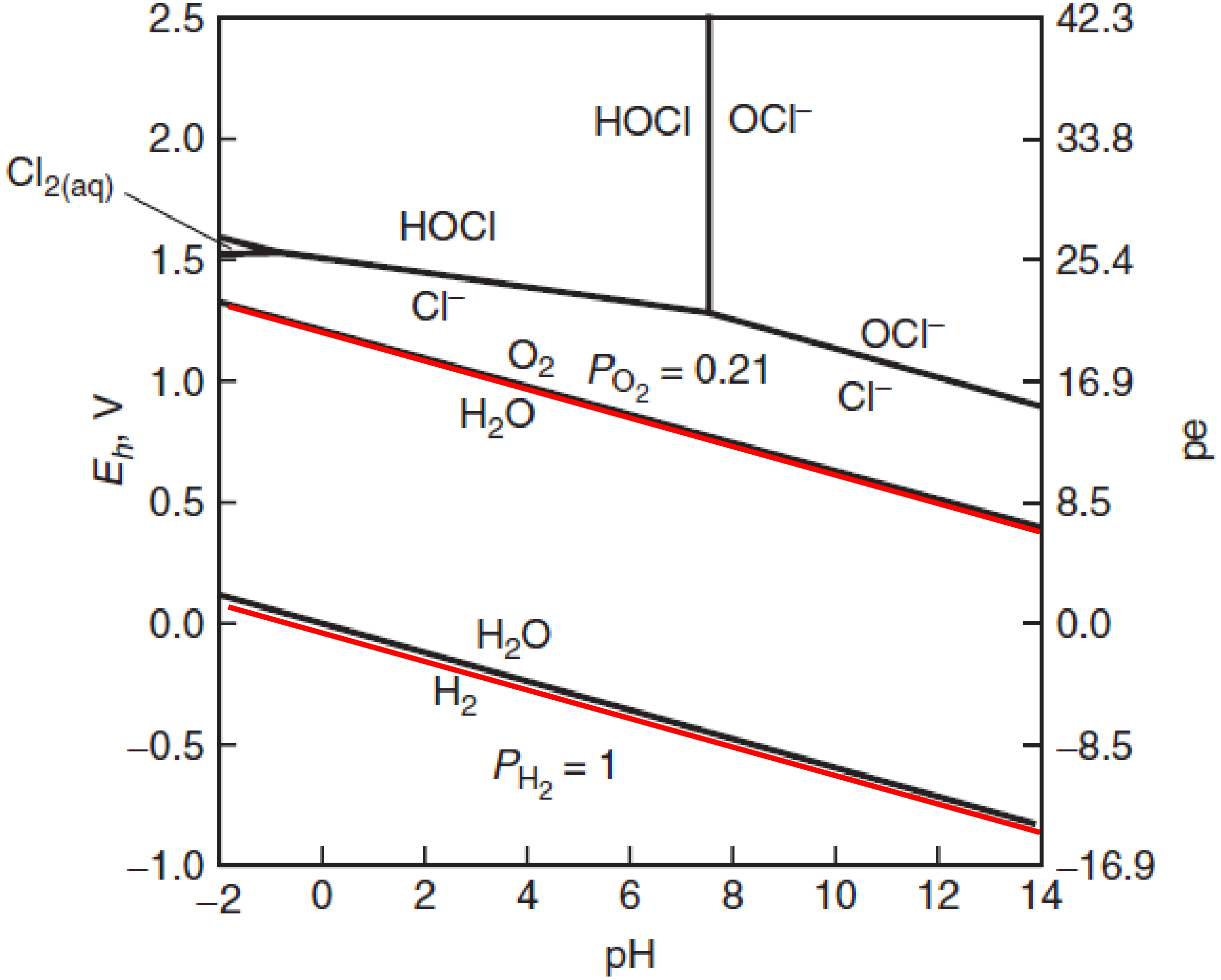


Figure 8-2
Predominance area diagram for chlorine system with total chlorine species concentration $C_{T,Cl}$ of 10^{-4} mol/L ($C_{T,Cl} = 10^{-4}$ mol/L $= 2[Cl_2(aq)] + [HOCl] + [OCl^-] + [Cl^-]$).

✓ CHLORINE SPECIES

$$C_{T,\mathrm{Cl}} = 10^{-4}\ \mathrm{M} = 2[\mathrm{Cl_2(aq)}] + [\mathrm{HOCl}] + [\mathrm{OCl^-}] + [\mathrm{Cl^-}] \tag{8-39}$$

$$\mathrm{Cl_2(aq) + H_2O \rightleftarrows Cl^- + HOCl + H^+} \tag{8-40}$$

$$\mathrm{HOCl \rightleftarrows H^+ + OCl^-} \qquad \mathrm{p}K_a = 7.5 \text{ at } 25^\circ\mathrm{C} \tag{8-41}$$

$$\mathrm{2HOCl + 2H^+ + 2e^- \rightleftarrows Cl_2(aq) + 2H_2O} \qquad E^\circ = 1.61\ \mathrm{V} \tag{8-44}$$

$$E_H = E^\circ - \frac{0.059}{2}\log\left\{\frac{[\mathrm{Cl_{2(aq)}}]}{[\mathrm{H^+}]^2[\mathrm{HOCl}]^2}\right\} \tag{8-45}$$

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, and Eq. 8-45 can be rewritten as

$$E_H = 1.61 - \frac{0.059}{2}\left\{2\mathrm{pH} + \log\left[\frac{3.33 \times 10^{-5}}{\left(3.33 \times 10^{-5}\right)^2}\right]\right\} \tag{8-46}$$

$$= 1.47 - 0.059\ \mathrm{pH} \quad \mathbf{(1)} \tag{8-47}$$

$$Cl_2(aq) + 2e^- \rightleftarrows 2Cl^- \qquad E^\circ = 1.396\ \text{V} \tag{8-48}$$

$$E_H = E^\circ - \frac{0.059}{2}\log\left(\frac{[Cl^-]^2}{[Cl_2(aq)]}\right) \tag{8-49}$$

Similarly, at the boundary $[Cl^-]$ equals $[Cl_2(aq)]$, and when Cl^- and $Cl_2(aq)$ predominate in the solution, $C_{T,Cl} \approx 2[Cl_2(aq)] + [Cl^-] = 10^{-4}$ M and $[Cl^-] = [Cl_2(aq)] = 3.33 \times 10^{-5}$ M, and Eq. 8-49 can be rewritten as

$$E_H = 1.52\ \text{V} \quad \textbf{(2)} \tag{8-50}$$

$$HOCl + H^+ + 2e^- \rightleftarrows Cl^- + H_2O \tag{8-55}$$

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

$$
\begin{array}{ll}
2HOCl + 2H^+ + 2e^- \rightleftarrows Cl_2(aq) + 2H_2O & E^\circ_{\text{red}} = 1.61\ \text{V} \\
Cl_2(aq) + 2e^- \rightleftarrows 2Cl^- & E^\circ_{\text{red}} = 1.396\ \text{V} \\
\hline
HOCl + H^+ + 2e^- \rightleftarrows Cl^- + H_2O & E^\circ_{\text{red,sum}} = ?
\end{array}
$$

The value of $E^\circ_{\text{red,sum}}$ can be computed using Eq. 8-21:

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

The E_H can be determined using the expression

$$E_H = E^\circ - \frac{0.059}{2}\log\left(\frac{[Cl^-]}{[HOCl][H^+]}\right) \tag{8-56}$$

At the boundary, $[Cl^-]$ equals $[HOCl]$ and Eq. 8-56 may be rewritten as

$$E_H = 1.50 - \frac{0.059}{2}\text{pH} \quad \textbf{(3)} \tag{8-57}$$

$$OCl^- + 2H^+ + 2e^- \rightleftarrows Cl^- + H_2O \qquad (8\text{-}58)$$

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

The value of $\Delta G^\circ_{Rxn,1}$ for the reaction involving hypochlorous acid can be determined using Eq. 8-18, rewritten as follows:

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

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

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

The value of $\Delta G^\circ_{Rxn,OCl^-}$ for the reaction involving the hypochlorite ion can be determined using Eq. 8-23, rewritten as follows:

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

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

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

The value of $\Delta G^\circ_{Rxn,sum}$ can be obtained using Eq. 8-18 as follows:

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

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

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

The value of $E^\circ_{\text{red,sum}}$ can be obtained by rearranging Eq. 8-18:

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

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

The E_H can be determined from the equation

$$E_H = E^\circ - \frac{0.059}{2}\log\left(\frac{[\text{Cl}^-]}{[\text{OCl}^-][\text{H}^+]^2}\right) \qquad (8\text{-}59)$$

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

(4)

$$E_H = 1.72 - 0.059\ \text{pH} \qquad (8\text{-}60)$$

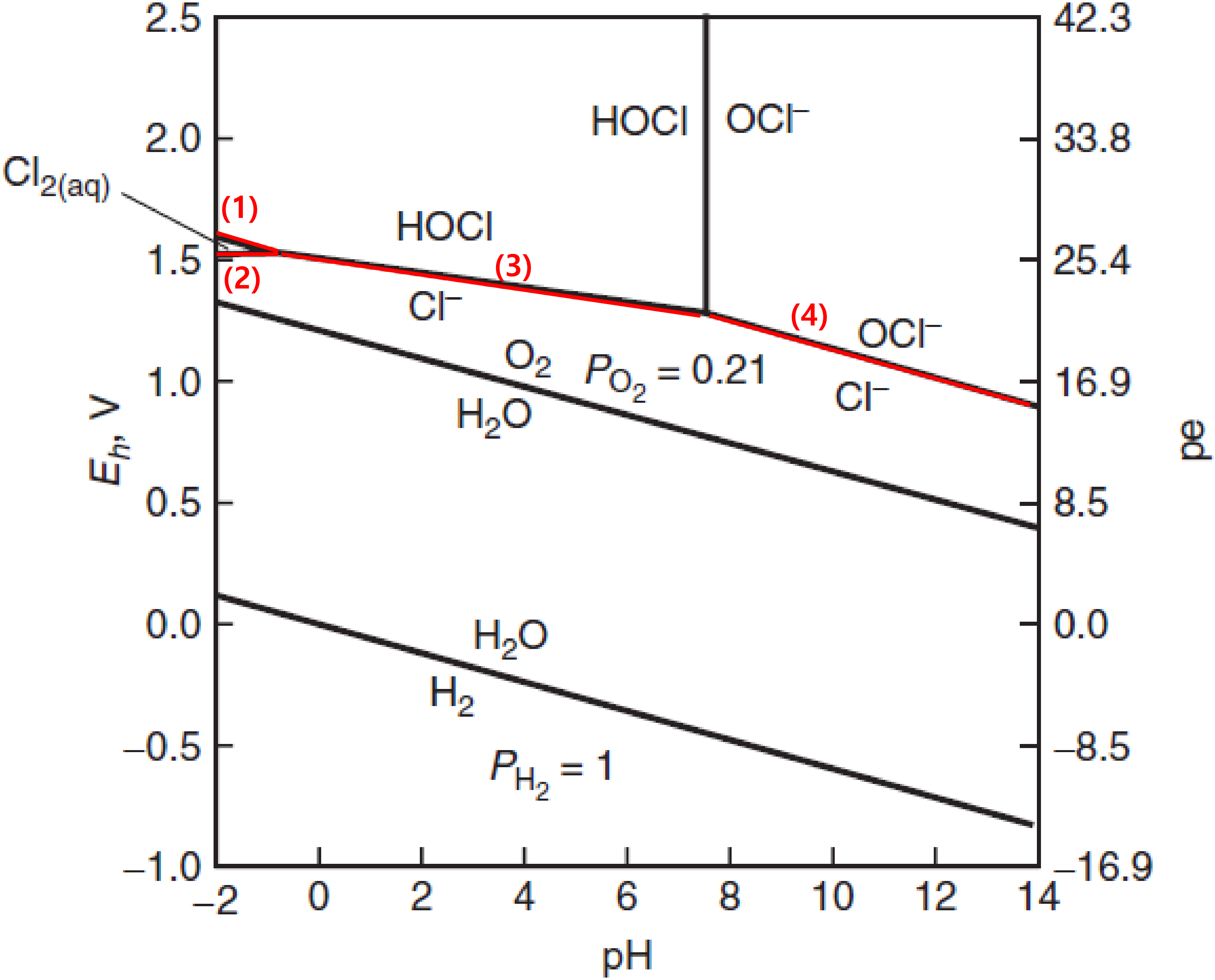


Figure 8-2
Predominance area diagram for chlorine system with total chlorine species concentration $C_{T,Cl}$ of 10^{-4} mol/L ($C_{T,Cl} = 10^{-4}$ mol/L $= 2[Cl_2(aq)] + [HOCl] + [OCl^-] + [Cl^-]$).

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

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:

$$\mathrm{R} + \text{oxidant}\ \left(\text{electron acceptor}, \mathrm{O_2}, \mathrm{O_3}, \mathrm{HO\bullet}\right) \rightarrow \text{intermediate by-products} \tag{8-61}$$

$$\text{intermediate by-products} + \text{oxidant} \rightarrow \mathrm{CO_2} + \mathrm{H_2O} + \text{mineral acids}\left(\text{e.g., HCl}\right) \tag{8-62}$$

$$r_{\mathrm{R}} = -k_{\mathrm{ox}} C_{\mathrm{ox}} C_{\mathrm{R}} \tag{8-63}$$

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

8-3 Conventional Chemical Oxidants

- ✓ Oxidation rate

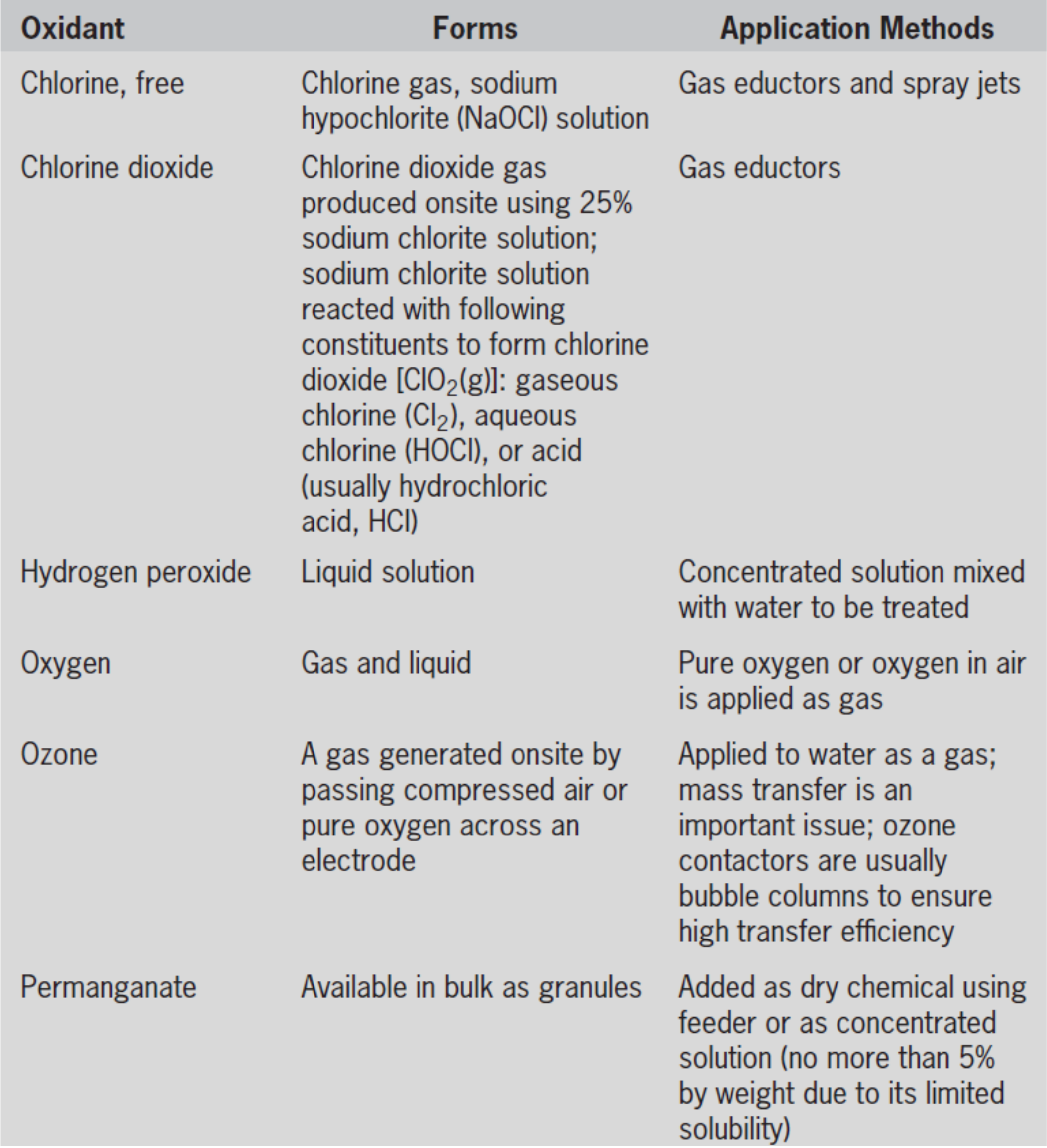
$$HO\bullet > O_3 > H_2O_2$$

$$> HOCl > ClO_2 > KMnO_4$$

$$> Cl_2 > O_2$$

Table 8-4

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)

Table 8-5

Properties of common oxidizing agents: chlorine, chlorine dioxide, ozone, hydrogen peroxide, and potassium permanganate

Property	Unit	Chlorine, Cl_2	Chlorine dioxide, ClO_2	Ozone, O_3	Hydrogen peroxide, H_2O_2	Potassium permanganate, $KMnO_4$
Molecular weight	g/mol	70.91	67.45	48.0	34.02	158.04
Boiling point (liquid)	°C	−33.97	11	−111.9 ± 0.3	114	
Melting point	°C	−100.98	−59	−192.5 ± 0.4	−50	150
Latent heat of vaporization at 0°C	kJ/kg	253.6	27.28	14.90		
Liquid density at 15.5°C	kg/m^3	1422.4	1640^a	1574	1460	
Solubility in water at 15.5°C	g/L	7.0	70.0^a	2.154		70
Specific gravity of liquid at 0°C (water = 1)	unitless	1.468		12.07	1.48	2.70
Vapor density at 0°C and 1 atm	kg/m^3	3.213	2.4	11	1.15	
Vapor density compared to dry air at 0°C and 1 atm	Unitless	2.486	1.856	1.666		
Specific volume of vapor at 0°C and 1 atm	m^3/kg	0.3112	0.417	0.464		
Critical temperature	°C	143.9	153	−12.1		
Critical pressure	kPa	7811.8		5532.3		

Source: Adapted in part from U.S. EPA (1986) and White (1999).

^{a}At 20°C.

Oxygen (O_2)

- ✓ Redox potential

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

- ✓ Applications

  - Oxidation of iron, manganese, and sulfides

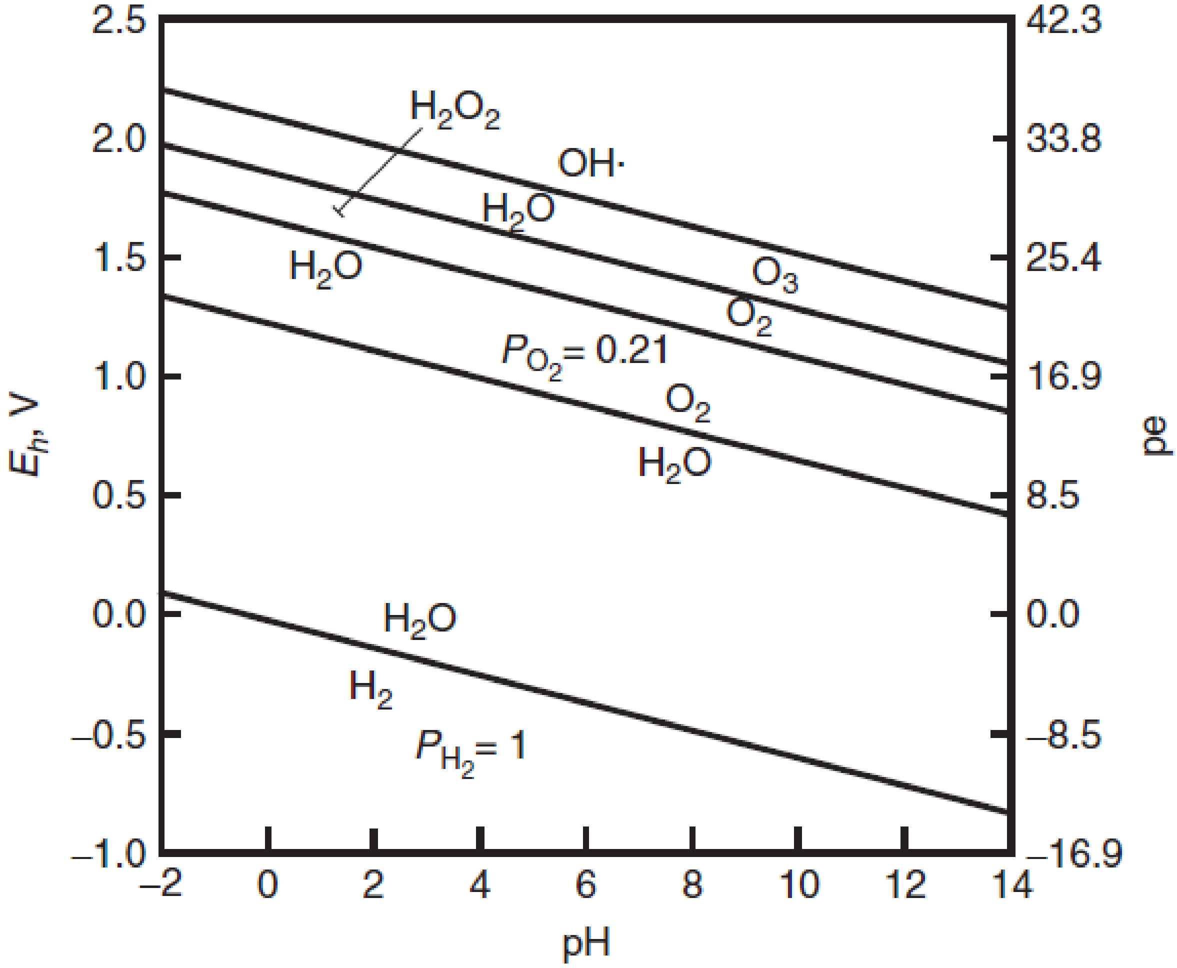


Figure 8-3
Predominance area diagram for oxygen system for oxygen concentration of 0.21 atm.

Example 8-7 Oxidation of Fe(II) in presence of oxygen

Bench-scale tests have been conducted to examine the rate of oxidation of Fe(II) in a particular well water in the presence of oxygen. The results are shown below:

Time, min	Fe(II), mg/L
0	5
8.3	0.55
16.7	0.30
24.8	0.19
41.7	0.05

Assuming that the partial pressure of oxygen is maintained at 0.21 atm during the tests, determine k_{app}.

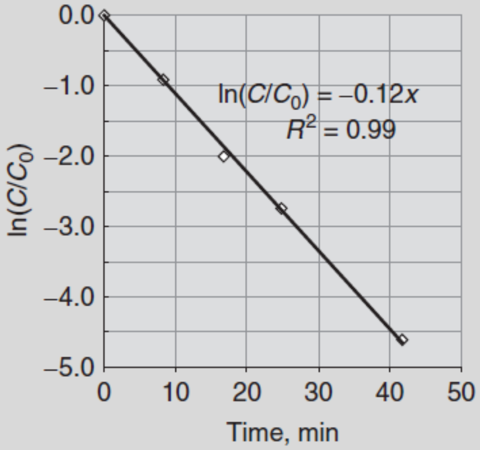
$$-\frac{d\,[\mathrm{Fe\,(II)}]}{dt} = -r_{\mathrm{Fe(II)}} = P_{\mathrm{O_2}}\,[\mathrm{Fe\,(II)}]\,k_{\text{app}} \qquad (8\text{-}67)$$

Solution

1. Set up a spreadsheet with the following columns:
   Column 1—time, min
   Column 2—concentration of Fe(II), mg/L
   Column 3—C/C_0
   Column 4—$\ln(C/C_0)$
   The spreadsheet values are given below:

Time, min	Fe(II), mg/L	Fe(II), C/C_0	Fe(II), $\ln(C/C_0)$
0	5	1	0.00
8.3	2.0	0.4	–0.92
16.7	0.67	0.134	–2.01
24.8	0.32	0.064	–2.75
41.7	0.05	0.01	–4.61

2. Plot time (column 1) versus $\ln(C/C_0)$ (column 4), and plot the best-fit regression line through the intercept at $t = 0$ and $\ln(C/C_0) = 0$.



The slope of the line is $-P_{O_2}k_{app}$:

$$P_{O_2}k_{app} = 0.12\ \text{min}^{-1}$$

$$k_{app} = \left(\frac{0.12/\text{min}}{0.11\ \text{atm}}\right) \simeq 1.091/\text{min}\cdot\text{atm}$$

Chlorine (Cl_2)

✓ Redox potential

$$Cl_2(aq) + 2e^- \rightleftarrows 2Cl^- \qquad E^\circ_{red} = 1.396\ V \qquad (8\text{-}70)$$

$$2HOCl + 2H^+ + 2e^- \rightleftarrows Cl_2(aq) + 2H_2O \qquad E^\circ_{red} = 1.61\ V \qquad (8\text{-}71)$$

$$HOCl + H^+ + 2e^- \rightleftarrows Cl^- + H_2O \qquad E^\circ_{red} = 1.50\ V \qquad (8\text{-}72)$$

$$OCl^- + H_2O + 2e^- \rightleftarrows Cl^- + 2OH^- \qquad E^\circ_{red} = 0.90\ V \qquad (8\text{-}73)$$

✓ 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

$$ClO_2\,(g) + 2H_2O + 5e^- \rightarrow Cl^- + 4OH^- \; E^\circ_{red} = 0.799\ V \qquad (8\text{-}78)$$

$$ClO_2 + e^- \rightarrow ClO_2^- \quad E^o_{red} = 0.95\sim1\ V$$

✓ Decomposition

$$2ClO_2 + 2OH^- \rightarrow ClO_2^- + ClO_3^- + H_2O \qquad (8\text{-}79)$$

✓ Applications

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

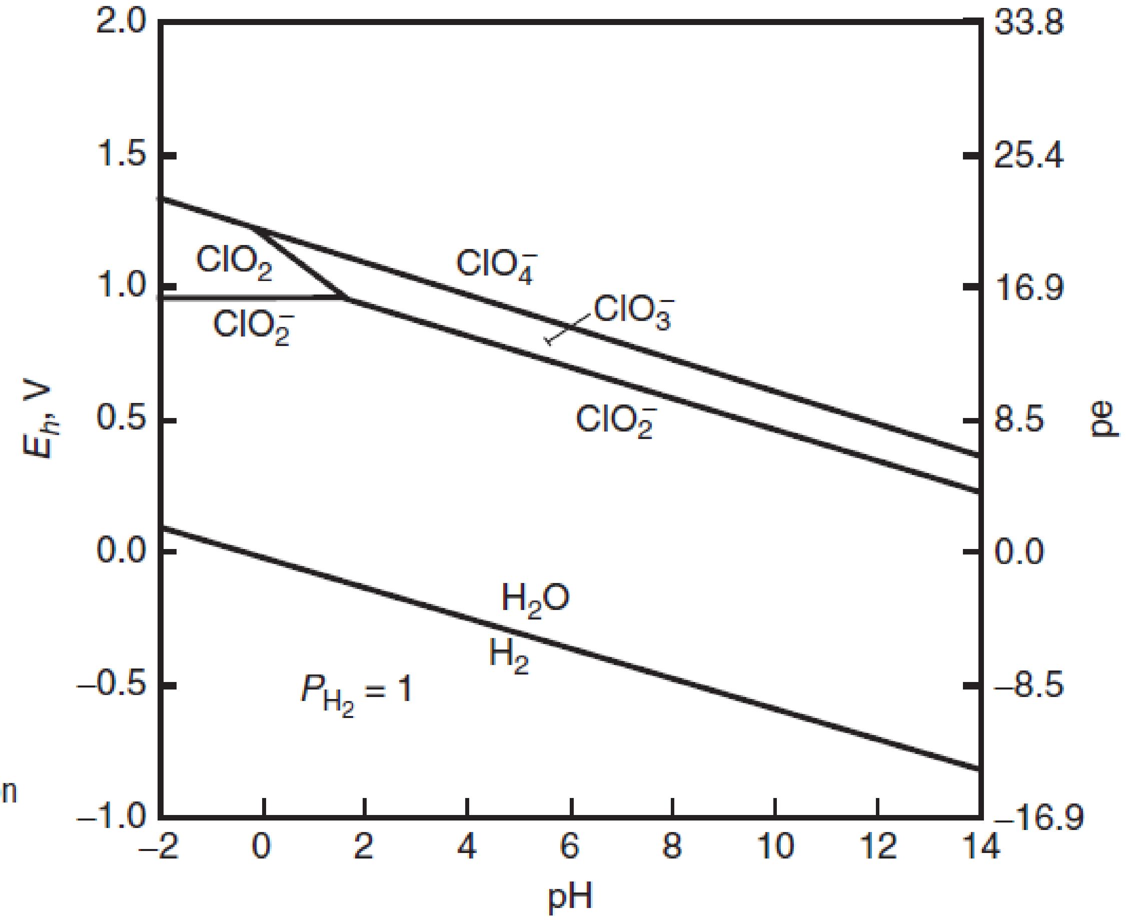


Figure 8-4
Predominance area diagram for chlorine dioxide system for total species concentration of 10^{-4} mol/L.

Hydrogen Peroxide (H_2O_2)

✓ Redox potential

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \qquad E^\circ_{\text{red}} = 1.780\ \text{V} \qquad (8\text{-}80)$$

✓ 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

$$O_3\,(g) + 2H^+ + 2e^- \rightarrow O_2 + H_2O \qquad E^\circ_{\text{red}} = 2.08\text{ V} \qquad (8\text{-}83)$$

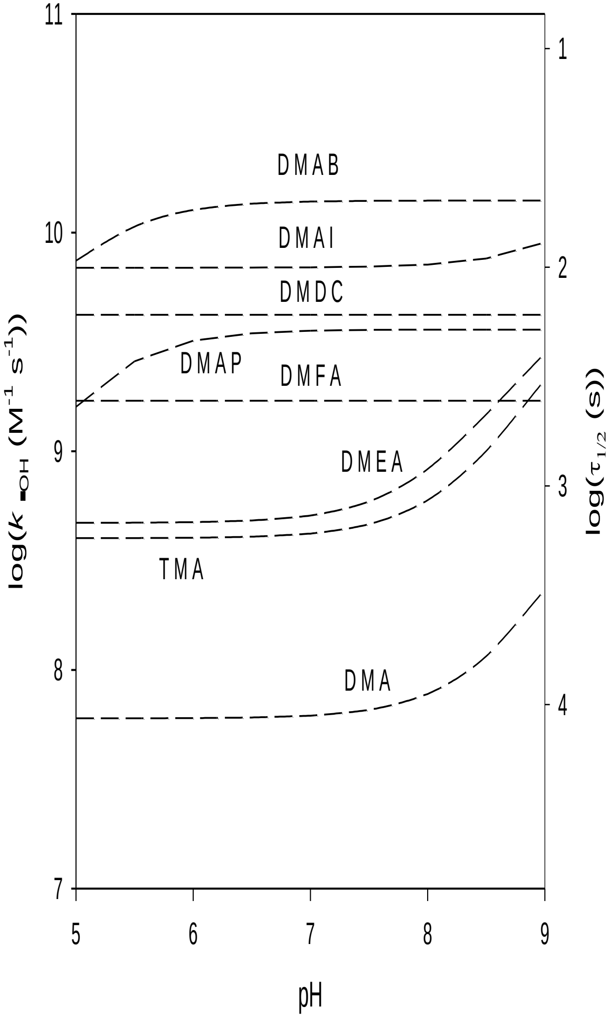
✓ Applications

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

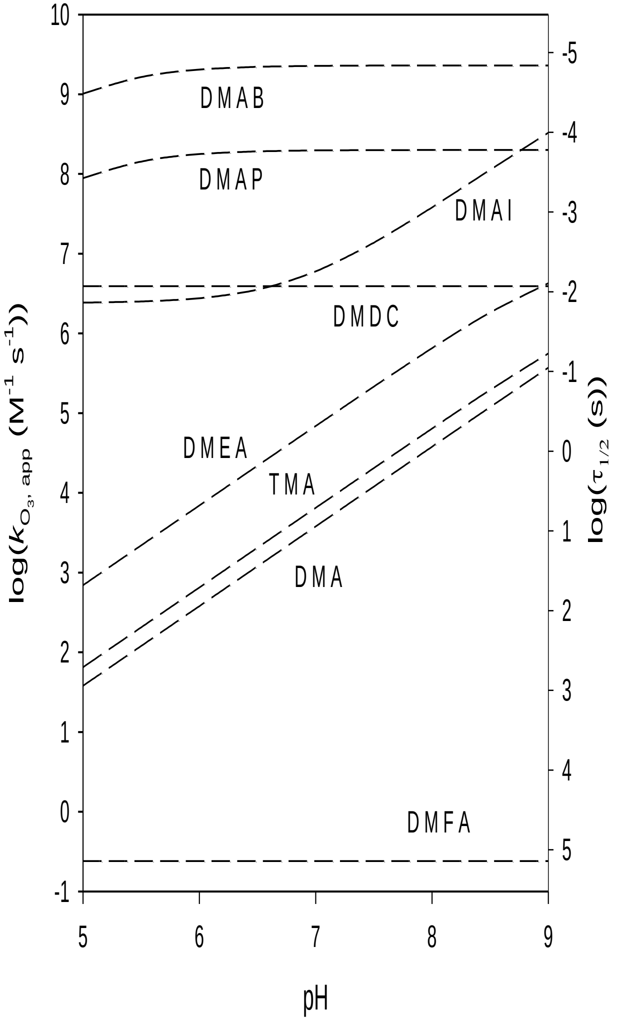
- A Reagent for advanced oxidation technology (a precursor of OH radical)
  e.g., UV/O_3, O_3/H_2O_2, Fe(II)/O_3

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

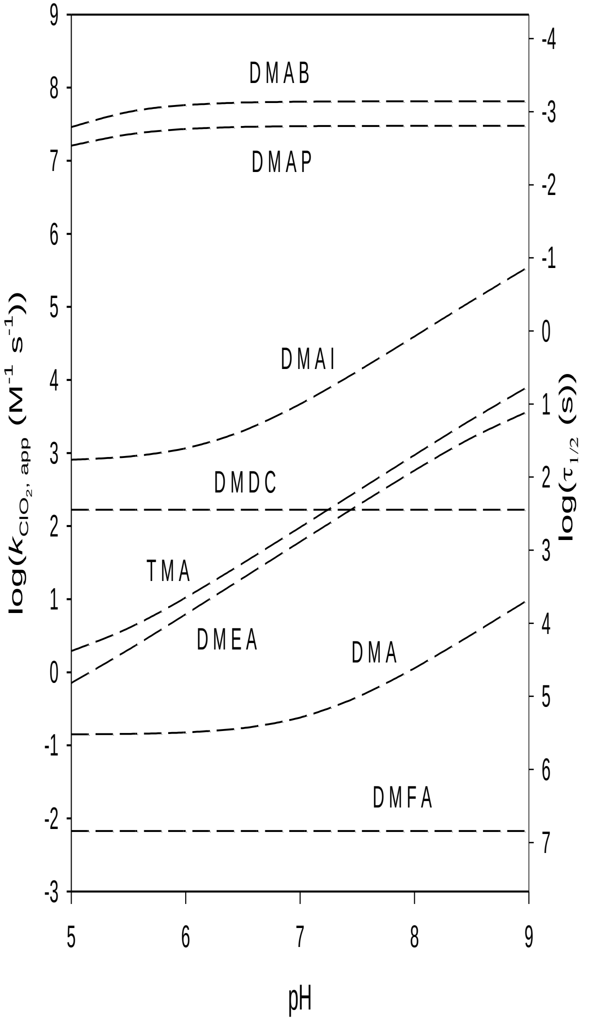
•OH



O_3



ClO_2



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

Permanganate (MnO_4^-)

✓ Redox potential

$$MnO_4^- + 4H^+ + 3e^- \rightleftarrows MnO_2\,(s) + 2H_2O \qquad E^\circ_{red} = 1.68\ V \qquad (8\text{-}87)$$

$$MnO_4^- + 8H^+ + 5e^- \rightleftarrows Mn^{2+} + 4H_2O \qquad E^\circ_{red} = 1.510\ V \qquad (8\text{-}88)$$

Under alkaline conditions the corresponding reduction half reaction is

$$MnO_4^- + 2H_2O + 3e^- \rightleftarrows MnO_2\,(s) + 4OH^- \qquad E^\circ_{red} = 0.590\ V \qquad (8\text{-}89)$$

✓ Applications

- Oxidation of iron, manganese, taste and odor compounds

- Pink color: needs dosage control

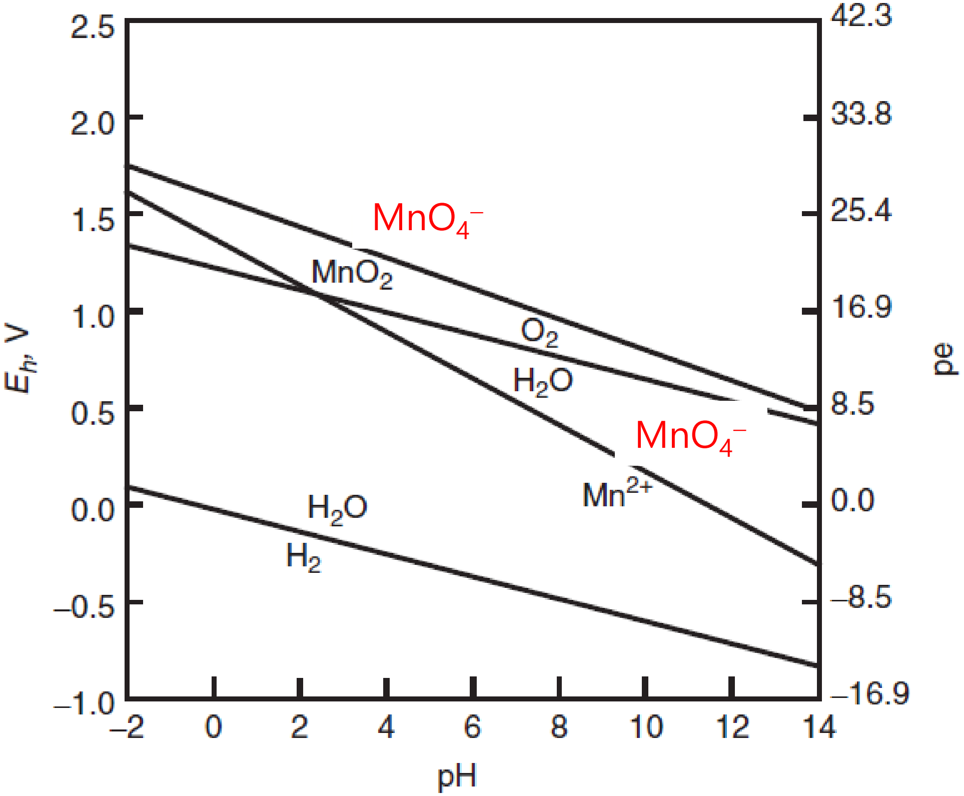


Figure 8-5
Predominance area diagram for permanganate system for total species concentration of 10^{-4} mol/L.

Example 8-8 Oxidation of Mn(II) with permanganate

Determine how much Mn(II) remains after 30 s of oxidation with permanganate in a CMBR. The initial concentrations of permanganate and Mn(II) are 1.5 times the stoichiometric requirement and 1 mg/L, respectively. Assume that the second-order rate constant is 10^5 L/mol · s.

*CMBR: Completely Mixed Batch Reactor

Solution

1. Calculate the initial concentration of permanganate using Eq. 8-91. Assume the initial concentrations of Mn^{2+} and MnO_4^{2-} are $C_{A\,0}$ and $C_{B\,0}$, respectively:

$$3Mn^{2+} + 2MnO_4^{-} + 2H_2O \rightarrow 5MnO_2 + 4H^{+}$$

$$C_{A0} = [Mn^{2+}]_0 = \frac{1 \times 10^{-3}\ \text{g/L}}{54.938\ \text{g/mol}} = 1.82 \times 10^{-5}\ \text{mol/L}$$

$$C_{B0} = [MnO_4^{-}]_0 = 1.5 \times \frac{2}{3} \times [Mn^{2+}]_0$$

$$= 1.5 \times \frac{2}{3} \times \left(1.82 \times 10^{-5}\ \text{mol/L}\right)$$

$$= 1.82 \times 10^{-5}\ \text{mol/L}$$

2. Calculate the remaining concentrations of Mn(II):

   a. Write a mass balance for a CMBR, and develop the rate expression:

$$\frac{dC_A}{dt} = r_A = -kC_AC_B = -kC_A\left[C_{B0} - \frac{2}{3}\left(C_{A0} - C_A\right)\right]$$

   b. Integrate the rate expression:

$$\frac{1}{C_{B0} - \frac{2}{3}C_{A0}} \int_{C_{A0}}^{C_A} \left[\frac{dC_A}{C_A} - \frac{d\left[C_{B0} - \frac{2}{3}\left(C_{A0} - C_A\right)\right]}{C_{B0} - \frac{2}{3}\left(C_{A0} - C_A\right)}\right] = -\int_0^t kdt$$

$$\frac{1}{C_{B0} - \frac{2}{3}C_{A0}} \ln\left(\frac{C_A}{C_{B0} - \frac{2}{3}\left(C_{A0} - C_A\right)} \times \frac{C_{B0}}{C_{A0}}\right) = -kt$$

$$\frac{C_A}{C_{B0} - \frac{2}{3}\left(C_{A0} - C_A\right)} = \frac{C_{A0}}{C_{B0}} \exp\left[-\left(C_{B0} - \frac{2}{3}C_{A0}\right)kt\right]$$

   c. Solve for Mn(II) concentration at t = 30 s:

$$\frac{C_A}{1.82 \times 10^{-5} - \frac{2}{3}\left(1.82 \times 10^{-5} - C_A\right)}$$

$$= \exp\left(-0.333 \times 1.82 \times 10^{-5} \times 10^5 \times 30\right)$$

$$C_A = [Mn^{2+}] = 7.56 \times 10^{-14}\ \text{M}$$