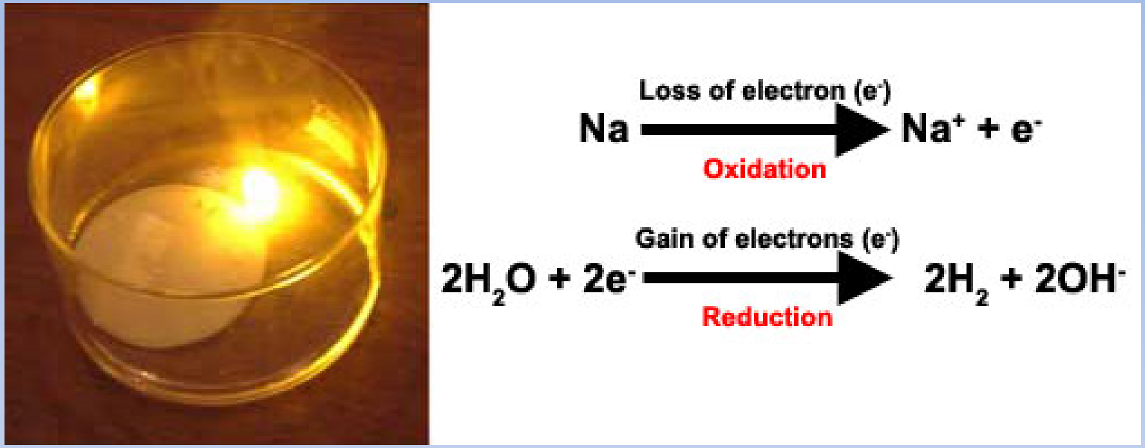
Redox reactions



$$\mathrm{Na} \xrightarrow[\text{Oxidation}]{\text{Loss of electron (e}^-\text{)}} \mathrm{Na}^+ + e^-$$

$$2H_2O + 2e^- \xrightarrow[\text{Reduction}]{\text{Gain of electrons (e}^-\text{)}} 2H_2 + 2OH^-$$

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Redox reactions

In a similar way that acids and bases have been defined as proton donors and proton acceptors, reductants and oxidants are defined as electron donors and electron acceptors. Because there are no free electrons, every oxidation reaction must be accompanied by a reduction, and vice versa; or an oxidant is a substance that causes oxidation to occur while being reduced itself.

One of the most significant of redox reactions in nature involves the weathering of pyrite according to:

$$4FeS_2 + 15O_2 + 14H_2O \rightarrow 4Fe(OH)_3 + 16H^+ + 8SO_4^{2-}$$

which probably proceeds by the following steps:

$$4FeS_2 + 14O_2 + 4H_2O \rightarrow 4Fe^{2+} + 8\,SO_4^{2-} + 8H^+$$
$$4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O$$
$$4Fe^{3+} + 12H_2O \rightarrow 4Fe(OH)_3 + 12H^+$$

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Oxidation of ferric (Fe^{2+}) compounds

Any ferrous compound, upon prolonged exposure to air is expected to oxidize, according to reactions of the form:

Olivine group

$$Fe_2SiO_4 + \tfrac{1}{2}O_2 + 2H_2O \rightarrow Fe_2O_3 + H_4SiO_4$$

Pyroxene

$$2CaFeSi_2O_6 \text{ (hedenbergite)} + 1/2O_2 + 10H_2O + 4CO_2 \rightarrow Fe_2O_3 + 4\,H_4SiO_4 + 2Ca^{2+} + 4HCO_3^-$$

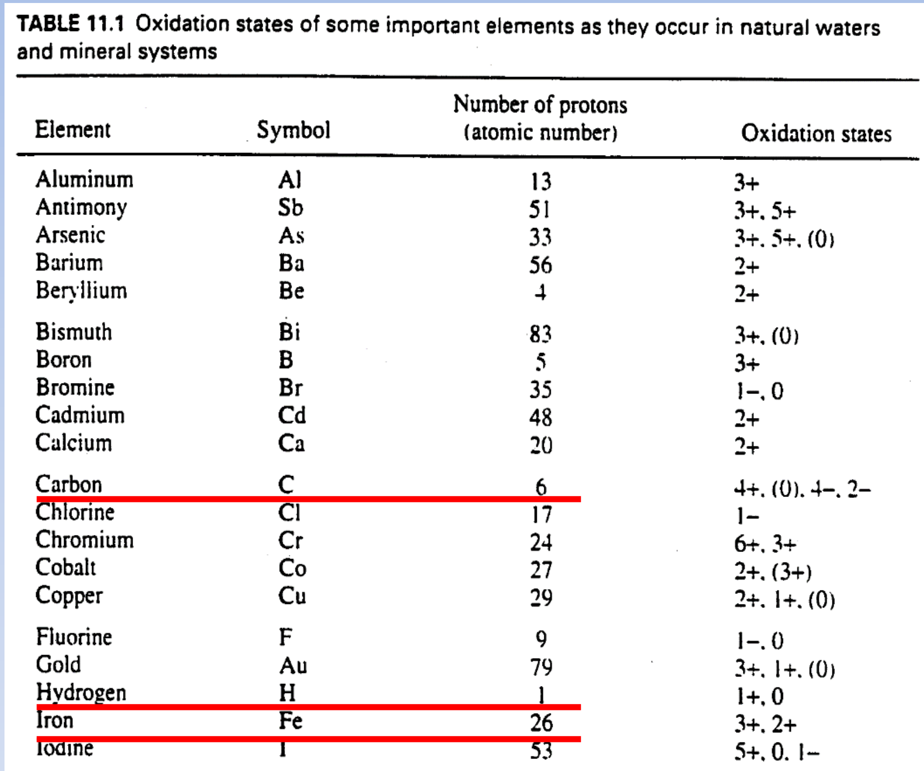
These equations express only the overall result of the oxidation process. Details of the mechanisms are not known, but most likely involve progressive dissolution of the ferrous compounds by H_2CO_3:

$$Fe_2SiO_4 + 4\,H_2CO_3 \leftarrow\rightarrow 2Fe^{2+} + 4HCO_3^- + H_4SiO_4$$

Followed by the oxidation of the Fe^{2+} by oxygen:

$$2Fe^{2+} + 4HCO_3^- + 1/2O_2 + 2H_2O \leftarrow\rightarrow Fe_2O_3 + 4H_2CO_3$$

Oxidation state of some important elements



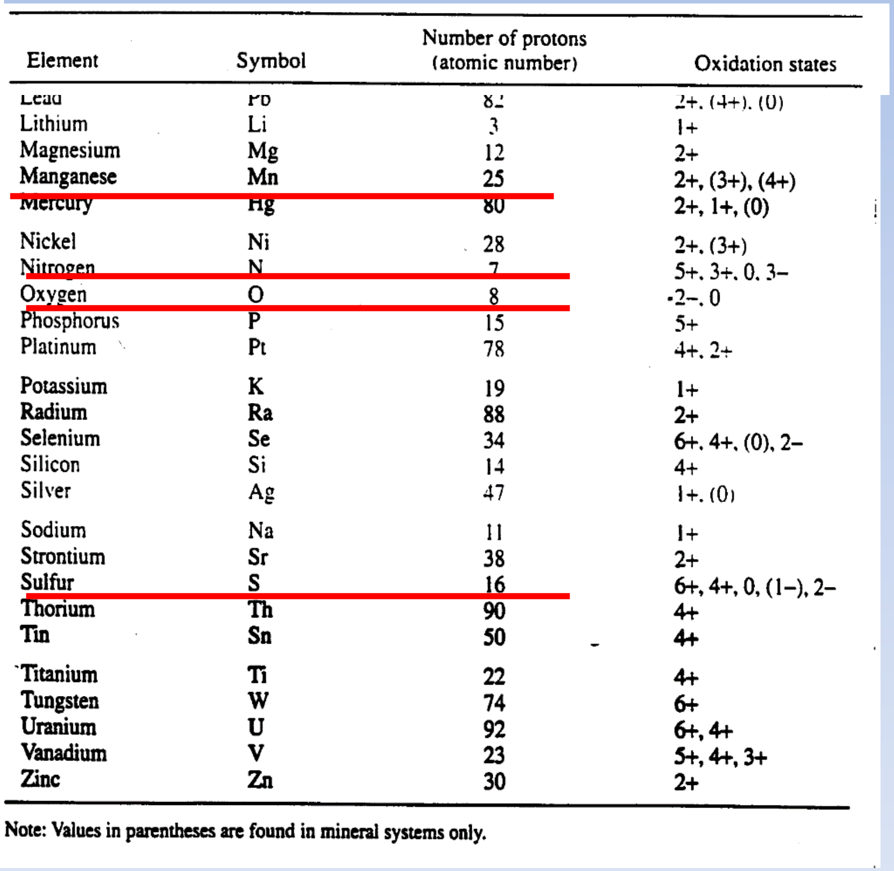


TABLE 11.1 Oxidation states of some important elements as they occur in natural waters and mineral systems

Element	Symbol	Number of protons (atomic number)	Oxidation states
Aluminum	Al	13	3+
Antimony	Sb	51	3+, 5+
Arsenic	As	33	3+, 5+, (0)
Barium	Ba	56	2+
Beryllium	Be	4	2+
Bismuth	Bi	83	3+, (0)
Boron	B	5	3+
Bromine	Br	35	1−, 0
Cadmium	Cd	48	2+
Calcium	Ca	20	2+
Carbon	C	6	4+, (0), 4−, 2−
Chlorine	Cl	17	1−
Chromium	Cr	24	6+, 3+
Cobalt	Co	27	2+, (3+)
Copper	Cu	29	2+, 1+, (0)
Fluorine	F	9	1−, 0
Gold	Au	79	3+, 1+, (0)
Hydrogen	H	1	1+, 0
Iron	Fe	26	3+, 2+
Iodine	I	53	5+, 0, 1−
Lead	Pb	82	2+, (4+), (0)
Lithium	Li	3	1+
Magnesium	Mg	12	2+
Manganese	Mn	25	2+, (3+), (4+)
Mercury	Hg	80	2+, 1+, (0)
Nickel	Ni	28	2+, (3+)
Nitrogen	N	7	5+, 3+, 0, 3−
Oxygen	O	8	2−, 0
Phosphorus	P	15	5+
Platinum	Pt	78	4+, 2+
Potassium	K	19	1+
Radium	Ra	88	2+
Selenium	Se	34	6+, 4+, (0), 2−
Silicon	Si	14	4+
Silver	Ag	47	1+, (0)
Sodium	Na	11	1+
Strontium	Sr	38	2+
Sulfur	S	16	6+, 4+, 0, (1−), 2−
Thorium	Th	90	4+
Tin	Sn	50	4+
Titanium	Ti	22	4+
Tungsten	W	74	6+
Uranium	U	92	6+, 4+
Vanadium	V	23	5+, 4+, 3+
Zinc	Zn	30	2+

Note: Values in parentheses are found in mineral systems only.

Redox equilibria and electron activity

Any oxidation or reduction reaction can be written as a half-cell reaction. The general half-reaction is, by convention, written as a reduction reaction with the electrons on the left:

$$aA + bB + n\text{é} \leftarrow\rightarrow cC + dD$$

where the upper case and lowercase letters denote the species involved in the reaction and their stoichiometric coefficients, and n is the number of electrons (é). Even though free electrons do not exist in solution, we can formulate an equilibrium expression for the half-cell:

$$K_{eq} = ((C)^c\,(D)^d)/((A)^a\,(B)^b\,(\text{é})^n) \quad \text{or}$$

$$\log K_{eq} = c\log(C) + d\log(D) - a\log(A) - b\log(B) - n\log(\text{é})$$

$$\begin{aligned} -\log(\text{é}) = p\varepsilon &= (1/n)\log K_{eq} - (1/n)\log\{((C)^c\,(D)^d)/((A)^a\,(B)^b)\} \\ &= (1/n)\log K_{eq} - (1/n)\log(\Pi(\text{reductants})^\nu/\,\Pi(\text{oxidants})^\nu) \\ &= (1/n)\log K_{eq} + (1/n)\log(\Pi(\text{oxidants})^\nu/\,\Pi(\text{reductants})^\nu) \\ &= p\varepsilon^o - (1/n)\log\{((C)^c\,(D)^d)/((A)^a\,(B)^b)\} \end{aligned}$$

Electron activity and the Nernst equation

$$p\varepsilon^o = 1/n \log K^o_{eq} = -(1/n)\,\Delta G^o_{rx}/2.303RT = E^o_h/(2.303\ RTF^{-1})$$

or $$\Delta G^o_{rx} = -RT \ln K^o_{eq} = -2.303\ RTn\ p\varepsilon^o = -nFE^o_h$$

thus,

$$E_h = E^o_h - 2.303\ (RT/nF) \cdot \log (C)^c(D)^d/(A)^a\ (B)^b$$

where E^o_h is the equilibrium redox potential (volts, w/r SHE), related to the free energy of the reaction, R is the gas constant, T is the absolute temperature and F is the Faraday constant = 96,490 C mol^{-1}.

The term (2.303RT/F) is called the Nernst factor and is equal to 0.05916 volts at 25°C. The above expression is know as the **Nernst equation**.

The Electrochemical Series

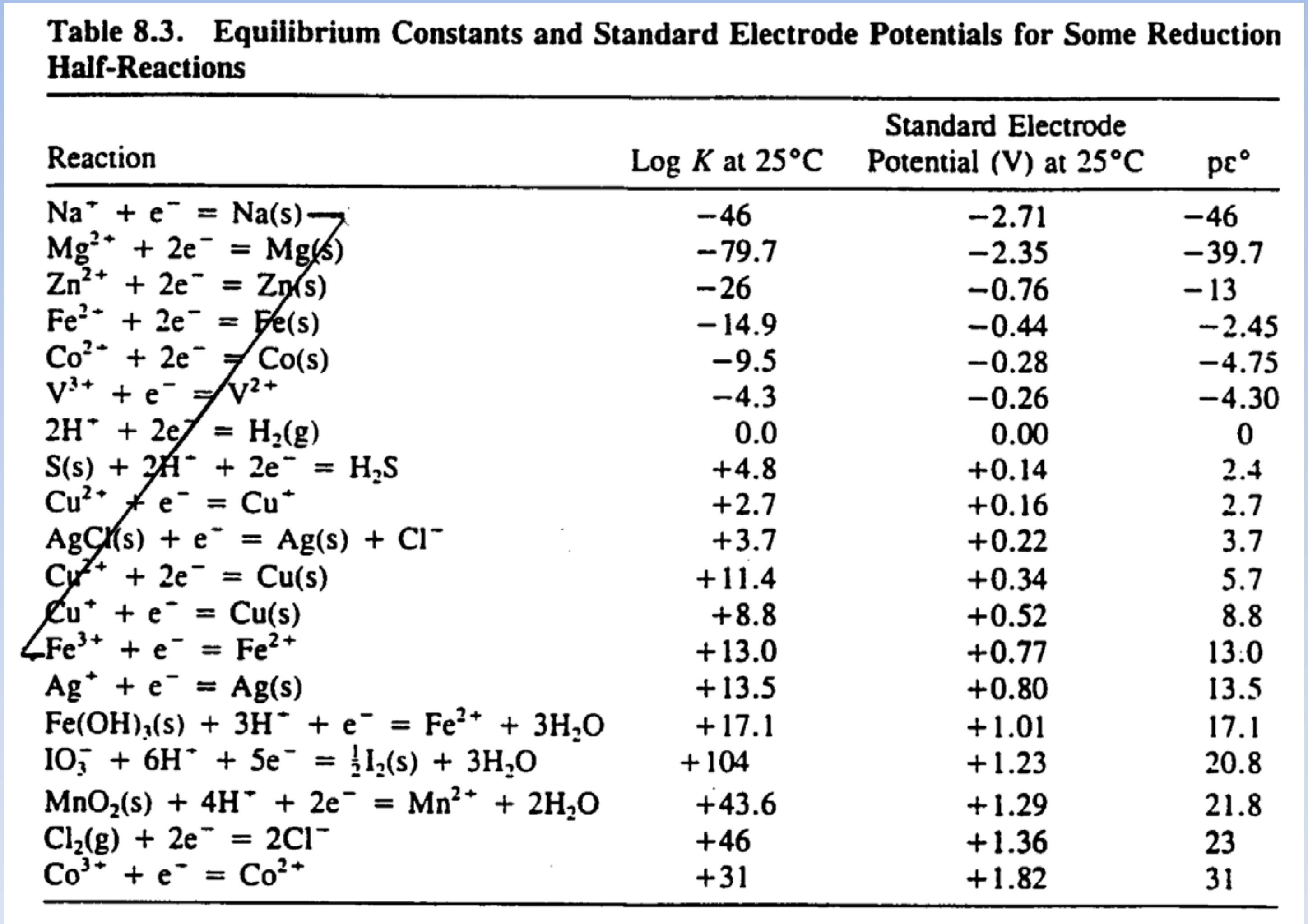
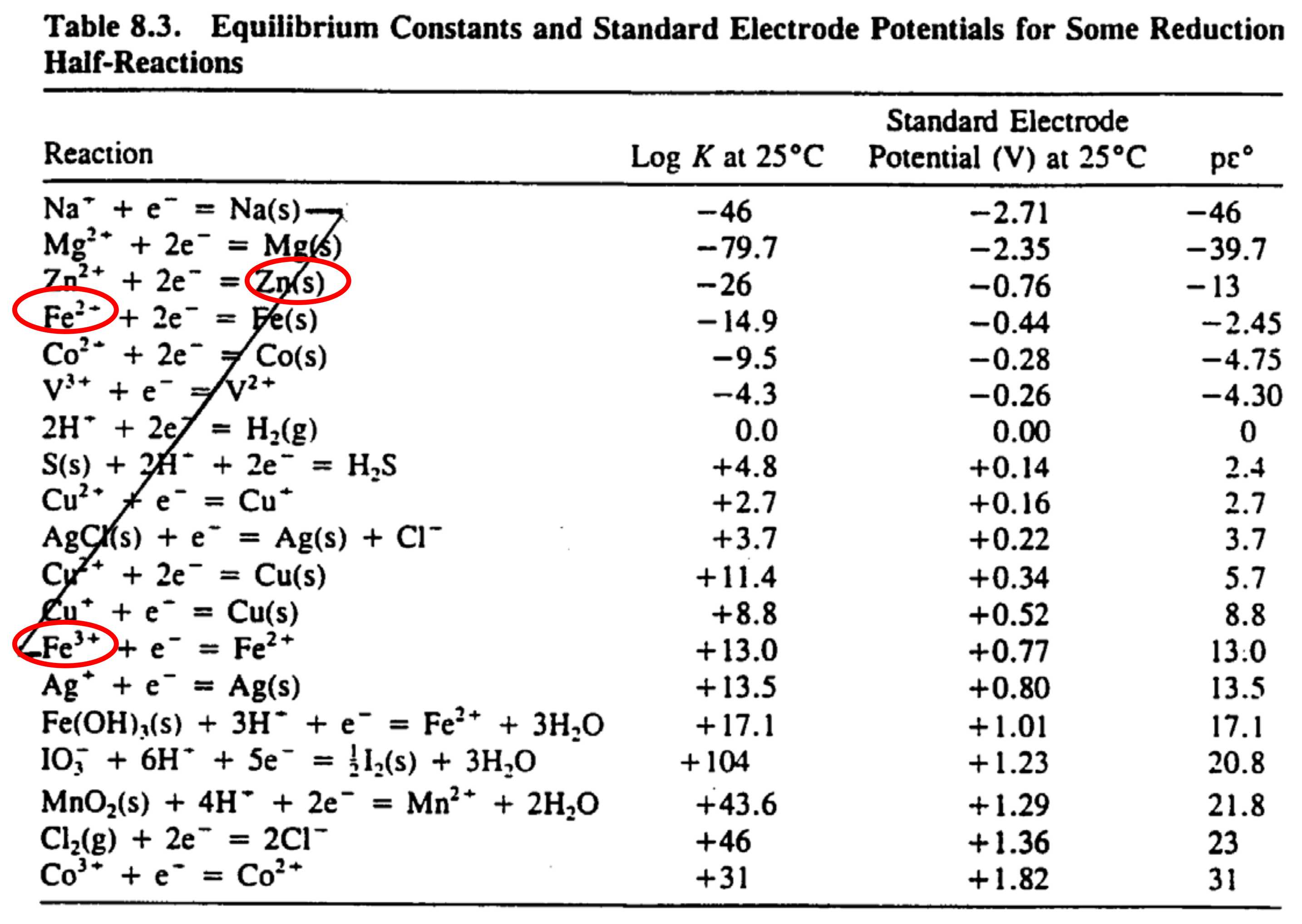


Table 8.3. Equilibrium Constants and Standard Electrode Potentials for Some Reduction Half-Reactions

Reaction	Log *K* at 25°C	Standard Electrode Potential (V) at 25°C	pε°
$Na^+ + e^- = Na(s)$	−46	−2.71	−46
$Mg^{2+} + 2e^- = Mg(s)$	−79.7	−2.35	−39.7
$Zn^{2+} + 2e^- = Zn(s)$	−26	−0.76	−13
$Fe^{2+} + 2e^- = Fe(s)$	−14.9	−0.44	−2.45
$Co^{2+} + 2e^- = Co(s)$	−9.5	−0.28	−4.75
$V^{3+} + e^- = V^{2+}$	−4.3	−0.26	−4.30
$2H^+ + 2e^- = H_2(g)$	0.0	0.00	0
$S(s) + 2H^+ + 2e^- = H_2S$	+4.8	+0.14	2.4
$Cu^{2+} + e^- = Cu^+$	+2.7	+0.16	2.7
$AgCl(s) + e^- = Ag(s) + Cl^-$	+3.7	+0.22	3.7
$Cu^{2+} + 2e^- = Cu(s)$	+11.4	+0.34	5.7
$Cu^+ + e^- = Cu(s)$	+8.8	+0.52	8.8
$Fe^{3+} + e^- = Fe^{2+}$	+13.0	+0.77	13.0
$Ag^+ + e^- = Ag(s)$	+13.5	+0.80	13.5
$Fe(OH)_3(s) + 3H^+ + e^- = Fe^{2+} + 3H_2O$	+17.1	+1.01	17.1
$IO_3^- + 6H^+ + 5e^- = \frac{1}{2}I_2(s) + 3H_2O$	+104	+1.23	20.8
$MnO_2(s) + 4H^+ + 2e^- = Mn^{2+} + 2H_2O$	+43.6	+1.29	21.8
$Cl_2(g) + 2e^- = 2Cl^-$	+46	+1.36	23
$Co^{3+} + e^- = Co^{2+}$	+31	+1.82	31

The Electrochemical Series



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$Fe^{2+} + 2e^- = Fe(s)$	−14.9	−0.44	−2.45
$Co^{2+} + 2e^- = Co(s)$	−9.5	−0.28	−4.75
$V^{3+} + e^- = V^{2+}$	−4.3	−0.26	−4.30
$2H^+ + 2e^- = H_2(g)$	0.0	0.00	0
$S(s) + 2H^+ + 2e^- = H_2S$	+4.8	+0.14	2.4
$Cu^{2+} + e^- = Cu^+$	+2.7	+0.16	2.7
$AgCl(s) + e^- = Ag(s) + Cl^-$	+3.7	+0.22	3.7
$Cu^{2+} + 2e^- = Cu(s)$	+11.4	+0.34	5.7
$Cu^+ + e^- = Cu(s)$	+8.8	+0.52	8.8
$Fe^{3+} + e^- = Fe^{2+}$	+13.0	+0.77	13.0
$Ag^+ + e^- = Ag(s)$	+13.5	+0.80	13.5
$Fe(OH)_3(s) + 3H^+ + e^- = Fe^{2+} + 3H_2O$	+17.1	+1.01	17.1
$IO_3^- + 6H^+ + 5e^- = \frac{1}{2}I_2(s) + 3H_2O$	+104	+1.23	20.8
$MnO_2(s) + 4H^+ + 2e^- = Mn^{2+} + 2H_2O$	+43.6	+1.29	21.8
$Cl_2(g) + 2e^- = 2Cl^-$	+46	+1.36	23
$Co^{3+} + e^- = Co^{2+}$	+31	+1.82	31

The Electrochemical Series

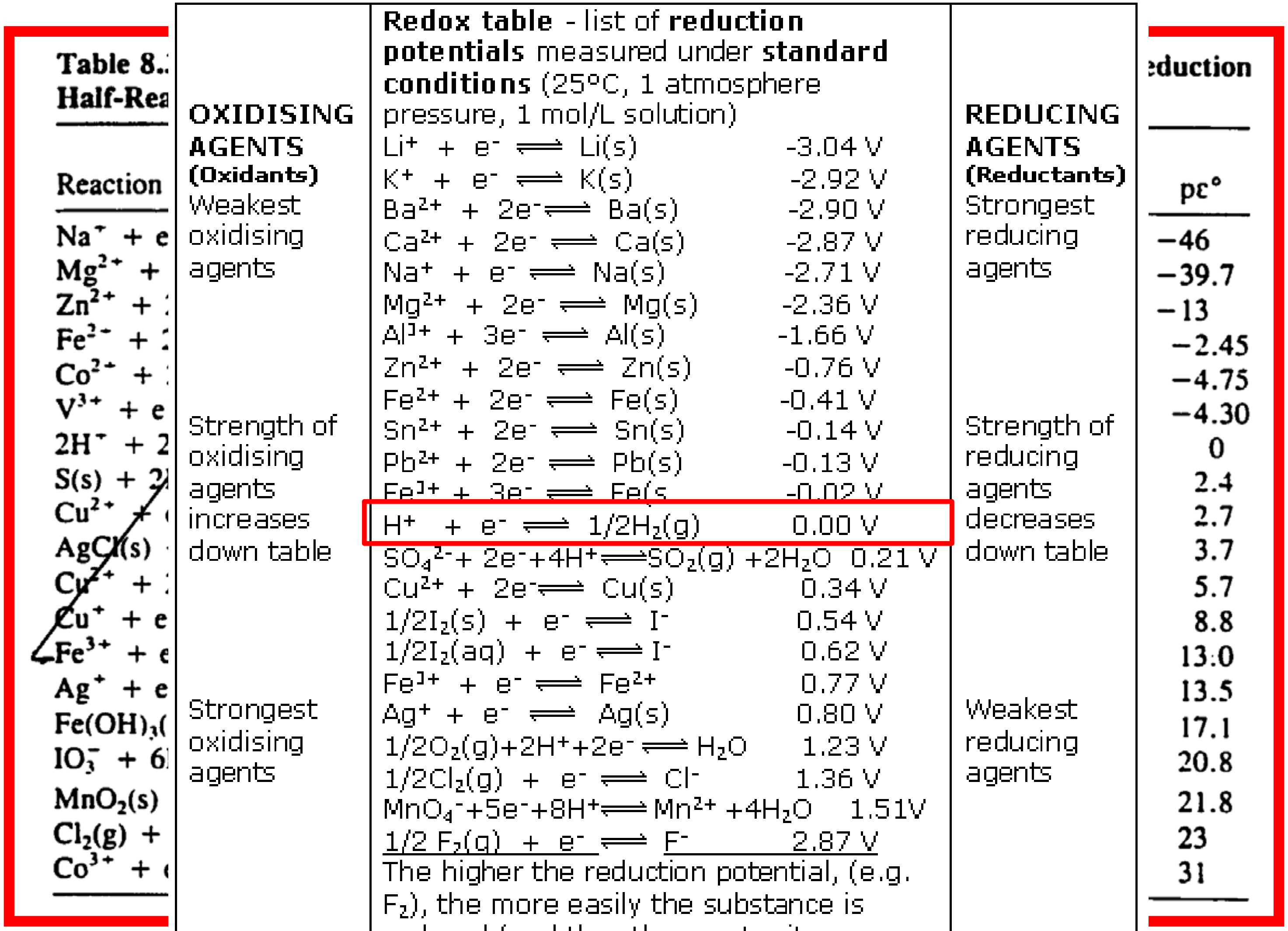


Table 8..
Half-Rea

Reaction	pε°
$Na^+ + e$	−46
Mg^{2+} +	−39.7
Zn^{2+} +	−13
Fe^{2+} +	−2.45
Co^{2+} +	−4.75
V^{3+} + e	−4.30
$2H^+$ + 2	0
S(s) + 2	2.4
Cu^{2+} +	2.7
AgCl(s)	3.7
Cu^{2+} +	5.7
Cu^+ + e	8.8
Fe^{3+} + e	13.0
Ag^+ + e	13.5
$Fe(OH)_3($	17.1
IO_3^- + 6	20.8
$MnO_2(s)$	21.8
$Cl_2(g)$ +	23
Co^{3+} +	31

OXIDISING AGENTS (Oxidants)

Weakest oxidising agents

Strength of oxidising agents increases down table

Strongest oxidising agents

Redox table - list of **reduction potentials** measured under **standard conditions** (25°C, 1 atmosphere pressure, 1 mol/L solution)

$Li^+ + e^- \rightleftharpoons Li(s)$	-3.04 V
$K^+ + e^- \rightleftharpoons K(s)$	-2.92 V
$Ba^{2+} + 2e^- \rightleftharpoons Ba(s)$	-2.90 V
$Ca^{2+} + 2e^- \rightleftharpoons Ca(s)$	-2.87 V
$Na^+ + e^- \rightleftharpoons Na(s)$	-2.71 V
$Mg^{2+} + 2e^- \rightleftharpoons Mg(s)$	-2.36 V
$Al^{3+} + 3e^- \rightleftharpoons Al(s)$	-1.66 V
$Zn^{2+} + 2e^- \rightleftharpoons Zn(s)$	-0.76 V
$Fe^{2+} + 2e^- \rightleftharpoons Fe(s)$	-0.41 V
$Sn^{2+} + 2e^- \rightleftharpoons Sn(s)$	-0.14 V
$Pb^{2+} + 2e^- \rightleftharpoons Pb(s)$	-0.13 V
$Fe^{3+} + 3e^- \rightleftharpoons Fe(s)$	-0.02 V
$H^+ + e^- \rightleftharpoons 1/2H_2(g)$	0.00 V
$SO_4^{2-} + 2e^- + 4H^+ \rightleftharpoons SO_2(g) + 2H_2O$	0.21 V
$Cu^{2+} + 2e^- \rightleftharpoons Cu(s)$	0.34 V
$1/2I_2(s) + e^- \rightleftharpoons I^-$	0.54 V
$1/2I_2(aq) + e^- \rightleftharpoons I^-$	0.62 V
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	0.77 V
$Ag^+ + e^- \rightleftharpoons Ag(s)$	0.80 V
$1/2O_2(g) + 2H^+ + 2e^- \rightleftharpoons H_2O$	1.23 V
$1/2Cl_2(g) + e^- \rightleftharpoons Cl^-$	1.36 V
$MnO_4^- + 5e^- + 8H^+ \rightleftharpoons Mn^{2+} + 4H_2O$	1.51V
$1/2\ F_2(g) + e^- \rightleftharpoons F^-$	2.87 V

The higher the reduction potential, (e.g. F_2), the more easily the substance is reduced (and thus the greater its oxidising power).

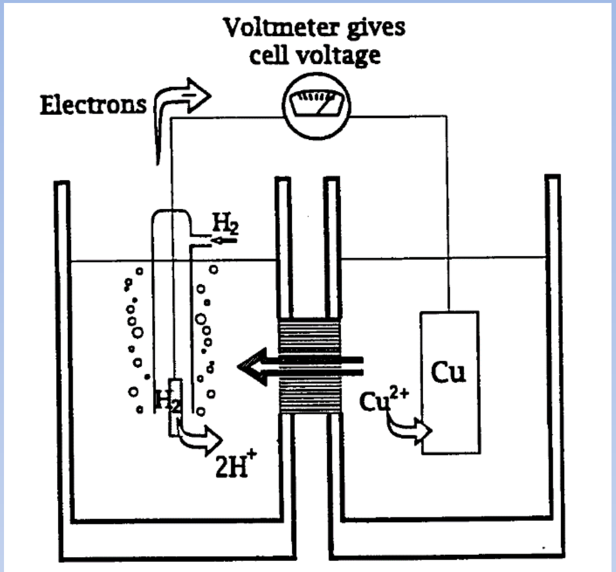
REDUCING AGENTS (Reductants)

Strongest reducing agents

Strength of reducing agents decreases down table

Weakest reducing agents

The Standard Hydrogen Electrode (SHE)



The electrode reaction for the H_2 gas-H^+ ion couple:

$$2H^+ + 2é = H_2(g)$$

for which $E_h = E^o + (RT/2F) \ln \{(H^+)^2/pH_2\}$

Since $E^o = -\Delta G^o_{rx}/nF$ and $\Delta G^o_{rx} = 0$, then $E^o = 0$.

$E_h = -0.0296 \log pH_2 – 0.0592$ pH
which is equal to 0 at $(H^+) = 1$ and $pH_2 = 1$

In a circuit such as the one presented here, it can measure the potential of:

$$Cu^{2+} + 2é \leftarrow\rightarrow Cu^o$$

The overall redox reaction is the sum of the two half-cell reactions or couples:

$$Cu^{2+} + H_2(g) \leftarrow\rightarrow 2H^+ + Cu^o$$

The measured E_h depends on the concentration of Cu^{2+} in the right-hand cell:

$$\begin{aligned} E_h \text{ (volts)} &= E_{reduction} - E_{oxidation} = E_{Cu2+/Cu} – E_{H2/H+} = E_{Cu2+/Cu} \\ &= E^o_h + (0.0592/2) \log (Cu^{2+}) \\ &= 0.340 + 0.0296 \log (Cu^{2+}) \end{aligned}$$

The standard state corresponds to E_h when the activity of all components = 1.

Galvanic cell

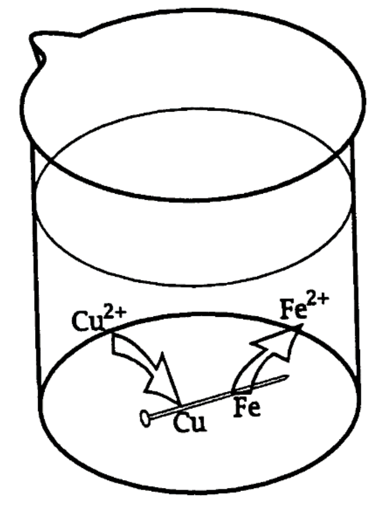
For the following reaction:

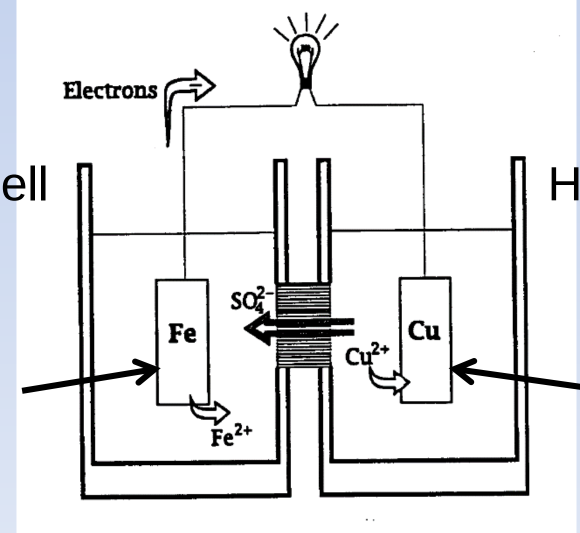
$$Fe(s) + Cu^{2+} \leftarrow\rightarrow Fe^{2+} + Cu(s)$$

The reaction can be broken up into two half cells:

$$1)\ Fe^{2+} + 2é \leftarrow\rightarrow Fe^{o} \quad E^{o}_{h} = -0.41V$$
$$2)\ Cu^{2+} + 2é \leftarrow\rightarrow Cu^{o} \quad E^{o}_{h} = +0.34V$$

If you do not have access to tables of E^{o}_{h}, you can calculate them from thermochemical data ($\Delta G^{o}_{rx} = -RT \ln K^{o}_{eq} = -nFE^{o}_{h}$).





Half-cell

Half-cell

anode

cathode

Galvanic cell: its standard potential

For example, for the first reaction:

$$\Delta G^o_{rx} = \Delta G^o_f\,(\mathrm{Fe(s)}) - \Delta G^o_f\,(\mathrm{Fe^{2+}})$$
$$= 0 - (-78900)\mathrm{J\ mol^{-1}} = 78900\ \mathrm{J\ mol^{-1}}$$
$$= -nF\,E^o_h = -2.303\ RTn\ p\varepsilon^o$$

$$E^o_h = -78900/(2x96485) = -0.41\mathrm{V}$$

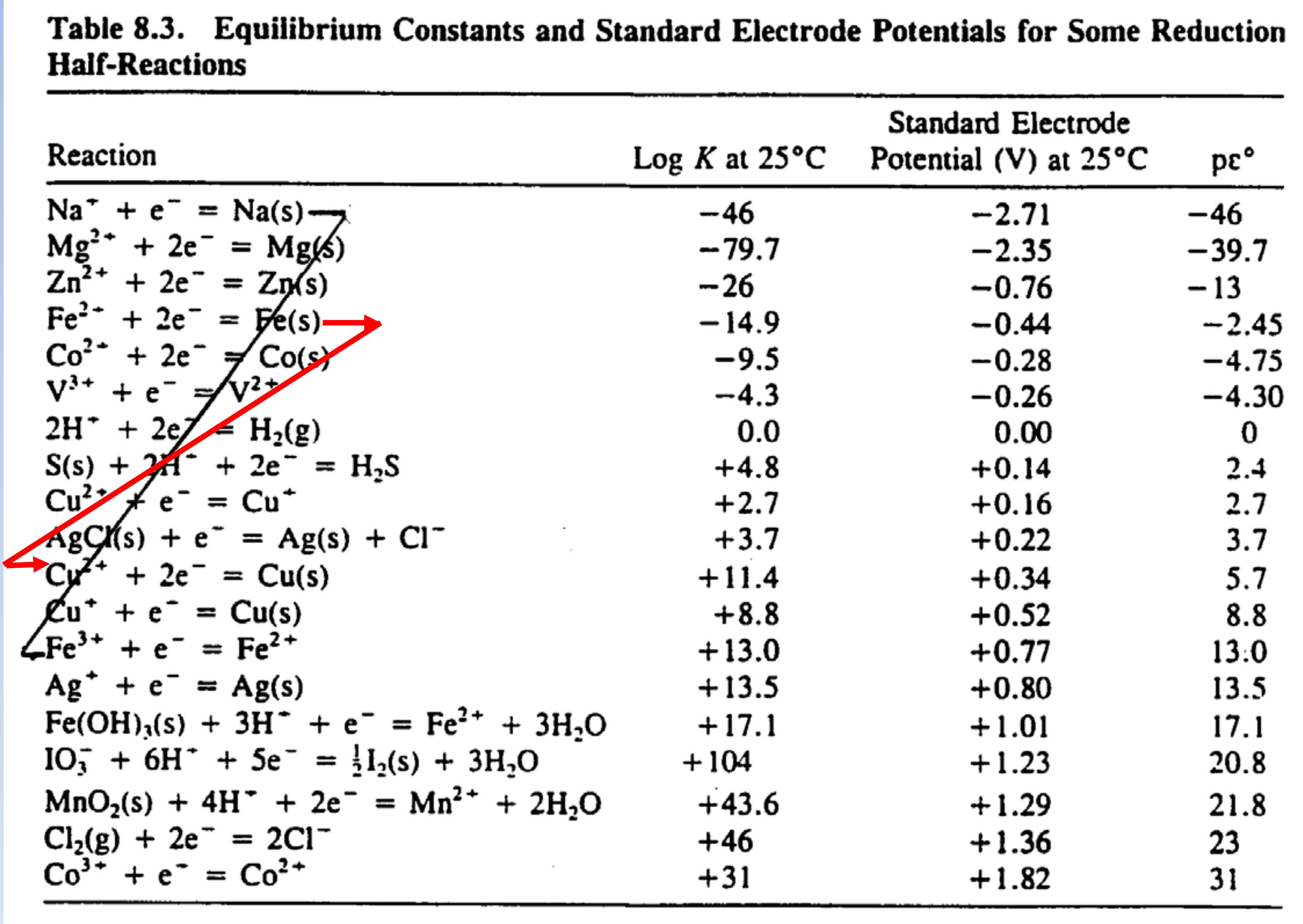
For the complete reaction:

$$E^o_{\text{Cu-Fe cell}} = E^o_{\text{reduction}} - E^o_{\text{oxidation}}$$
$$= E^o_{\text{Cu half-cell}} - E^o_{\text{Fe half-cell}}$$
$$= 0.34 - (-0.41)$$
$$= 0.75\mathrm{V}$$

The signs of both ΔG^o_{rx} and E^o of the complete cell reaction depend on how the cell is written, but the signs of the half-cell reactions do not. In this case, E^o is positive and therefore ΔG^o_{rx} is negative, meaning that the reactions should occur as written, i.e., $\mathrm{Fe(s)} + \mathrm{Cu^{2+}} \leftrightarrow \mathrm{Fe^{2+}} + \mathrm{Cu(s)}$

The potential calculated above is the standard potential when the activities of all the components are equal to one.

The Electrochemical Series



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$Mg^{2+} + 2e^- = Mg(s)$	−79.7	−2.35	−39.7
$Zn^{2+} + 2e^- = Zn(s)$	−26	−0.76	−13
$Fe^{2+} + 2e^- = Fe(s)$	−14.9	−0.44	−2.45
$Co^{2+} + 2e^- = Co(s)$	−9.5	−0.28	−4.75
$V^{3+} + e^- = V^{2+}$	−4.3	−0.26	−4.30
$2H^+ + 2e^- = H_2(g)$	0.0	0.00	0
$S(s) + 2H^+ + 2e^- = H_2S$	+4.8	+0.14	2.4
$Cu^{2+} + e^- = Cu^+$	+2.7	+0.16	2.7
$AgCl(s) + e^- = Ag(s) + Cl^-$	+3.7	+0.22	3.7
$Cu^{2+} + 2e^- = Cu(s)$	+11.4	+0.34	5.7
$Cu^+ + e^- = Cu(s)$	+8.8	+0.52	8.8
$Fe^{3+} + e^- = Fe^{2+}$	+13.0	+0.77	13.0
$Ag^+ + e^- = Ag(s)$	+13.5	+0.80	13.5
$Fe(OH)_3(s) + 3H^+ + e^- = Fe^{2+} + 3H_2O$	+17.1	+1.01	17.1
$IO_3^- + 6H^+ + 5e^- = \frac{1}{2}I_2(s) + 3H_2O$	+104	+1.23	20.8
$MnO_2(s) + 4H^+ + 2e^- = Mn^{2+} + 2H_2O$	+43.6	+1.29	21.8
$Cl_2(g) + 2e^- = 2Cl^-$	+46	+1.36	23
$Co^{3+} + e^- = Co^{2+}$	+31	+1.82	31

Galvanic cell: its true potential

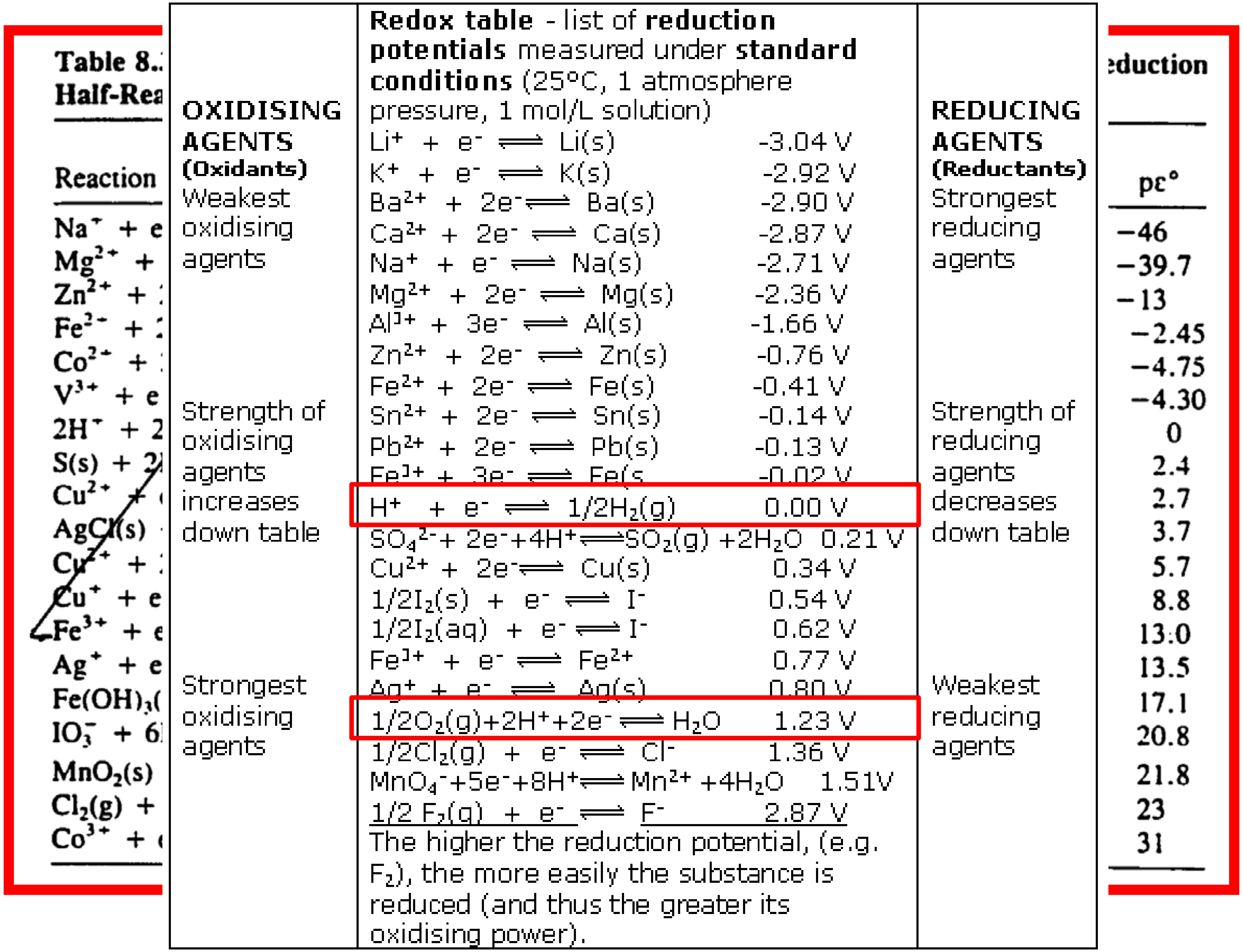
If not at standard state and $(Cu^{2+}) = 0.1$ and $(Fe^{2+}) = 1.5$.

Using the Nernst equation for the complete cell at 25°C, we obtain:

$$
\begin{aligned}
E_h &= E^o - 2.303\ (RT/nF)\ \log Q \\
&= E^o - (0.0592/n)\ \log\ (Fe^{2+})/(Cu^{2+}) \\
&= 0.75 - (0.0592/2)\ \log\ (1.5/0.1) \\
&= 0.75 - 0.035 \\
&= 0.715V
\end{aligned}
$$

Conversely, the E_h of an aqueous system can be used to calculate the ratio of the reduced and oxidized species in solution.

The Electrochemical Series



OXIDISING AGENTS (Oxidants)	Redox table - list of reduction potentials measured under standard conditions (25°C, 1 atmosphere pressure, 1 mol/L solution)		REDUCING AGENTS (Reductants)
	$Li^+ + e^- \rightleftharpoons Li(s)$	-3.04 V	
	$K^+ + e^- \rightleftharpoons K(s)$	-2.92 V	
Weakest oxidising agents	$Ba^{2+} + 2e^- \rightleftharpoons Ba(s)$	-2.90 V	Strongest reducing agents
	$Ca^{2+} + 2e^- \rightleftharpoons Ca(s)$	-2.87 V	
	$Na^+ + e^- \rightleftharpoons Na(s)$	-2.71 V	
	$Mg^{2+} + 2e^- \rightleftharpoons Mg(s)$	-2.36 V	
	$Al^{3+} + 3e^- \rightleftharpoons Al(s)$	-1.66 V	
	$Zn^{2+} + 2e^- \rightleftharpoons Zn(s)$	-0.76 V	
	$Fe^{2+} + 2e^- \rightleftharpoons Fe(s)$	-0.41 V	
Strength of oxidising agents increases down table	$Sn^{2+} + 2e^- \rightleftharpoons Sn(s)$	-0.14 V	Strength of reducing agents decreases down table
	$Pb^{2+} + 2e^- \rightleftharpoons Pb(s)$	-0.13 V	
	$Fe^{3+} + 3e^- \rightleftharpoons Fe(s$	-0.02 V	
	$H^+ + e^- \rightleftharpoons 1/2H_2(g)$	0.00 V	
	$SO_4^{2-} + 2e^- + 4H^+ \rightleftharpoons SO_2(g) + 2H_2O$	0.21 V	
	$Cu^{2+} + 2e^- \rightleftharpoons Cu(s)$	0.34 V	
	$1/2I_2(s) + e^- \rightleftharpoons I^-$	0.54 V	
	$1/2I_2(aq) + e^- \rightleftharpoons I^-$	0.62 V	
	$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	0.77 V	
Strongest oxidising agents	$Ag^+ + e^- \rightleftharpoons Ag(s)$	0.80 V	Weakest reducing agents
	$1/2O_2(g) + 2H^+ + 2e^- \rightleftharpoons H_2O$	1.23 V	
	$1/2Cl_2(g) + e^- \rightleftharpoons Cl^-$	1.36 V	
	$MnO_4^- + 5e^- + 8H^+ \rightleftharpoons Mn^{2+} + 4H_2O$	1.51V	
	$1/2\ F_2(g) + e^- \rightleftharpoons F^-$	2.87 V	

The higher the reduction potential, (e.g. F_2), the more easily the substance is reduced (and thus the greater its oxidising power).

Table 8.

Half-Rea

eduction

Reaction	pε°
$Na^+ + e$	−46
$Mg^{2+} +$	−39.7
$Zn^{2+} +$	−13
$Fe^{2+} +$	−2.45
$Co^{2+} +$	−4.75
$V^{3+} + e$	−4.30
$2H^+ + 2$	0
$S(s) + 2$	2.4
$Cu^{2+} +$	2.7
$AgCl(s)$	3.7
$Cu^{2+} +$	5.7
$Cu^+ + e$	8.8
$Fe^{3+} + e$	13.0
$Ag^+ + e$	13.5
$Fe(OH)_3($	17.1
$IO_3^- + 6$	20.8
$MnO_2(s)$	21.8
$Cl_2(g) +$	23
$Co^{3+} +$	31

Theoretical limits of stability in an aqueous solution

The upper boundary of the water stability field is defined by E_h and pH values for which liquid water is in equilibrium with O_2(g) at 1 bar pressure. It can be computed from the reaction:

$$O_2(g) + 4H^+ + 4\acute{e} \leftarrow\rightarrow 2\,H_2O \qquad E^o_h = +1.23V$$

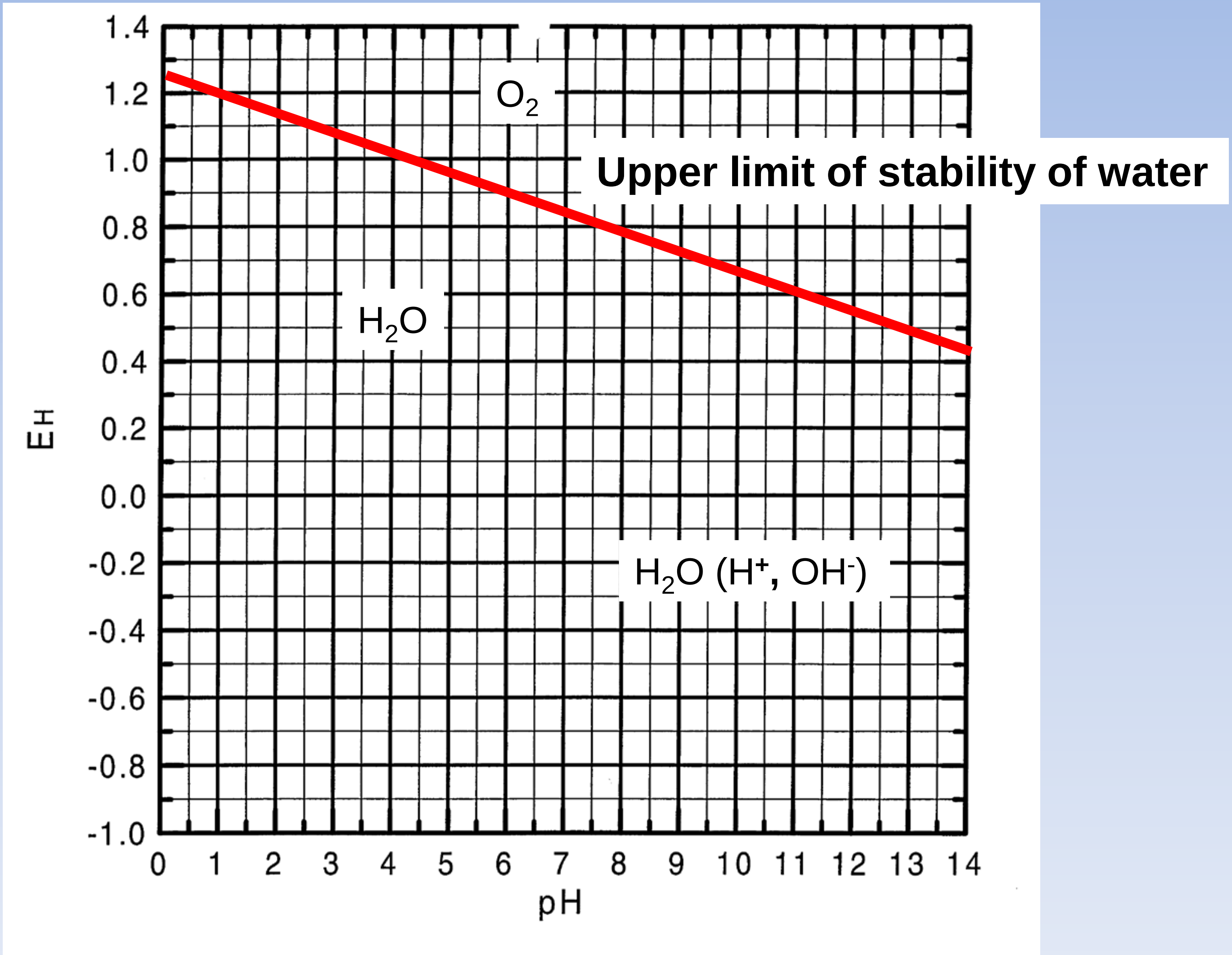
Therefore,

$$\begin{aligned} E_h &= 1.23 + (0.059/4)\log (H^+)^4\, pO_2 \\ &= 1.23 - 0.059\,pH + \underbrace{0.015\log(0.2)}_{\mathbf{-0.01}} \\ &= 1.22 - 0.059\,pH \end{aligned}$$

At the upper boundary where $pO_2(g) = 1$bar, the equation reduces to:

$$E_h\ (\text{volts}) = 1.23 - 0.0592\,pH$$

Eh vs pH diagram



Theoretical limits of stability in an aqueous solution

The lower boundary is defined by E_h and pH values for which liquid water is in equilibrium with $H_2(g)$ at 1 bar pressure. The lower limit of E_h within the stability field of water is described by the reduction of H_2O to hydrogen gas according to:

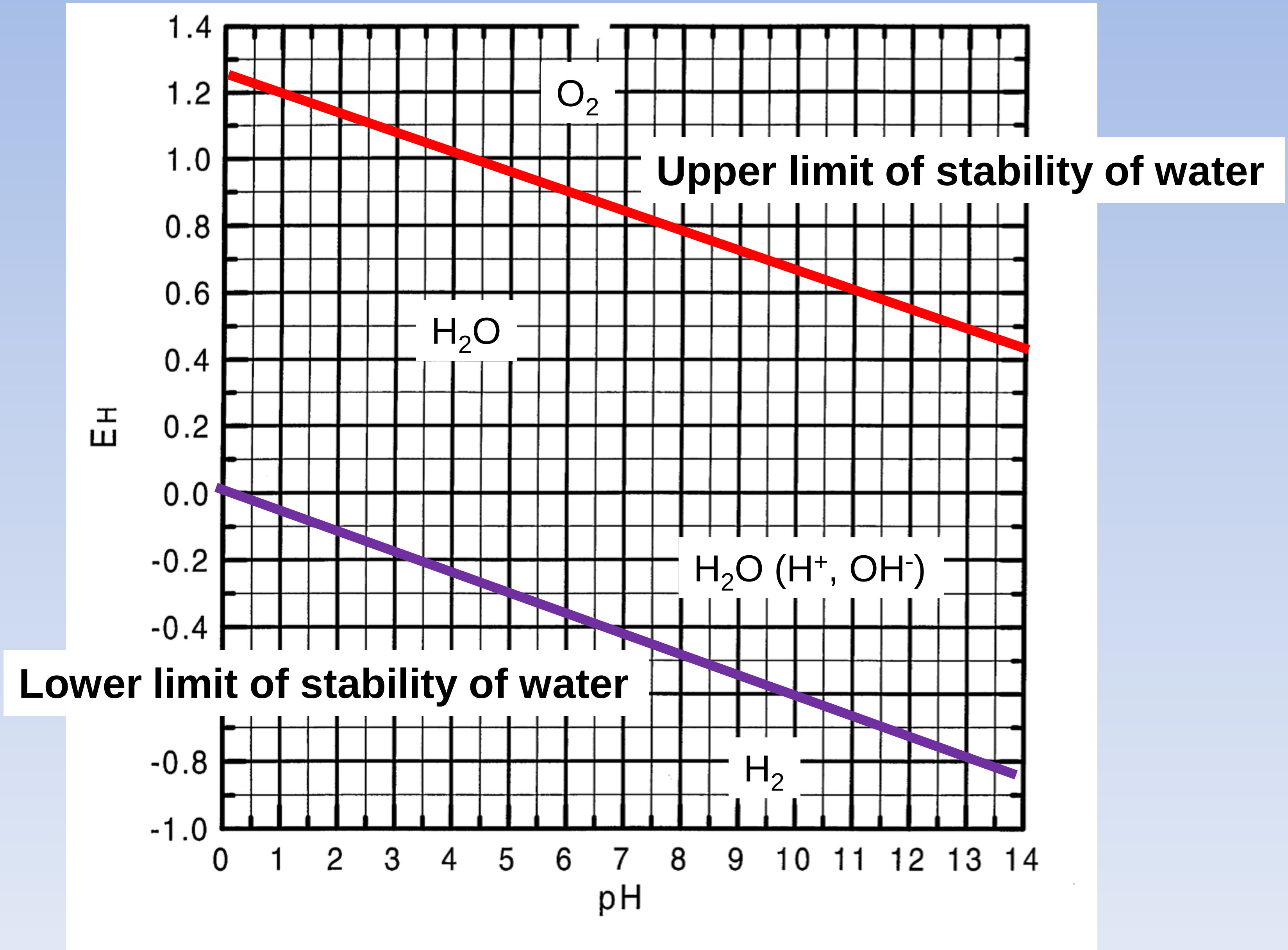
$$2H^+ + 2é \leftarrow\rightarrow H_2(g) \qquad E^o_h = 0.00V$$

$$E_h = 0.00 + (0.059/2) \log (H^+)/pH_2$$
$$= -0.059 \text{ pH} – (0.0059/2) \log pH_2$$

for a pH_2 of 1 atm, the lowest value of E_h is obtained:

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

Eh vs pH diagram



Practical measurements of E_h

The standard hydrogen electrode is the ultimate reference for E_h (and pH) measurements but is both impractical and cumbersome to use for routine measurements in the field and laboratory. Instead, these measurements are usually performed with a platinum or glassy carbon indicator electrode and a calomel (Hg_2Cl_2/Hg^o; E = 245 mV) or silver-silver chloride (Ag/AgCl; E = 200 mV) reference electrode. These reference electrodes have known potentials with respect to the SHE and measurements can be corrected accordingly:

$$E_h = E_{\text{measured}} + E_{\text{ref. Electrode}}$$

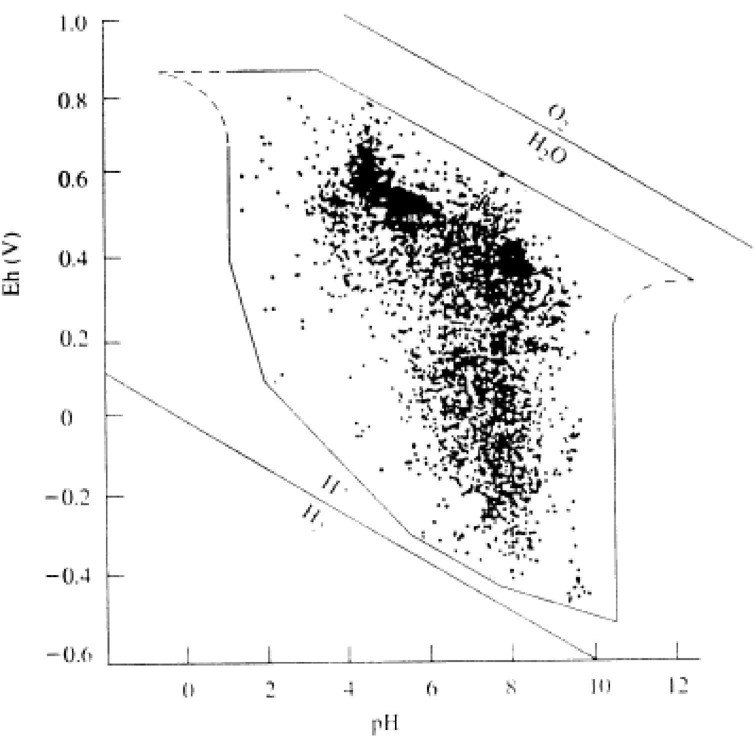
The performance of the electrodes can be verified using E_h buffers prepared in the laboratory from various ferrous-ferric iron salts (i.e., ZoBell's solutions).

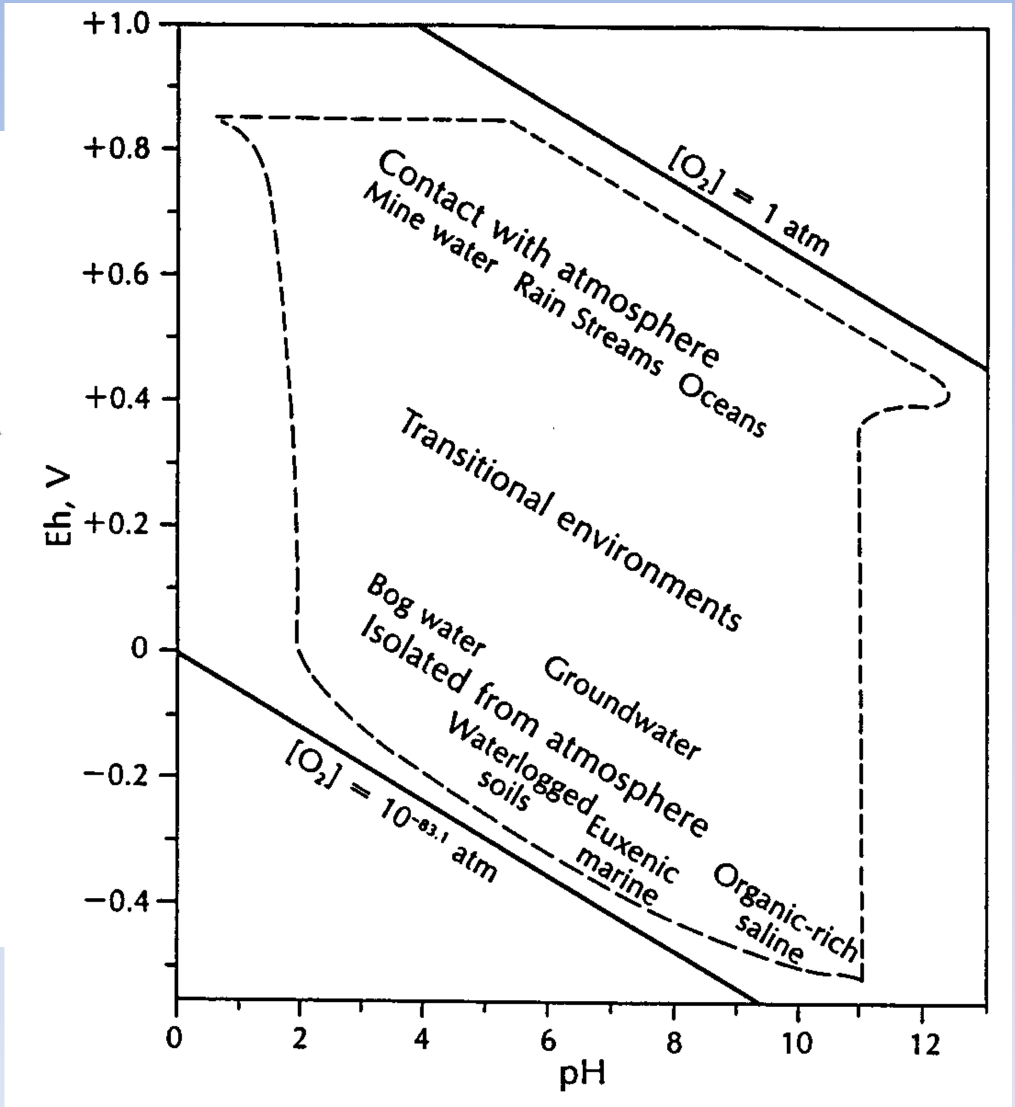
The controlling redox equilibrium in a ZoBell solution is:

$$Fe(CN)_6^{3-} + é \leftarrow\rightarrow Fe(CN)_6^{4-}$$

The E_h of an equimolar solution is 0.429 mV at 25°C or 0.229 mV w/r to a Ag/AgCl reference electrode.

Redox conditions in natural waters





Redox conditions in natural waters

The pε or E_h of oxygenated water is thought to be controlled by the concentration of dissolved oxygen, following the reaction:

$O_2(g) + 4H^+ + 4é \leftarrow\rightarrow 2\ H_2O(l)$ $\log K^o = 83.1,\ E^o{}_h = +1.23V,\ p\varepsilon = 20.8$

Hence,

$$\log K^o = 83.1 = 2 \log (H_2O) - \log pO_2 - 4 \log (H^+) - 4 \log (é)$$

$$= 2 (-0.01) - 0.69 + 4\ pH + 4\ p\varepsilon$$

at $pH = 7$, $p\varepsilon = 13.9$ or $E_h = + 0.83$ volts

In most well-oxygenated natural waters, the value of pε will not diverge significantly from this value. By taking into consideration hydrolysis and complexation (inorganic and organic) reactions and the formation of sparingly soluble minerals, one should be able to construct E_h-pH diagrams for most elements and determine the predominant species in oxygenated solutions.

Redox conditions in natural waters

The decomposition of organic matter accumulating in sediment and bottom waters isolated from atmospheric exchange by strong stratification of the water column may strip the water of oxygen and cause a fall in the pε or E_h . If the water becomes completely de-oxygenated (i.e., anoxic), sulfate-reducing bacteria will proliferate and lead to the production of H_2S. In anoxic systems, the E_h is believed to be controlled by either the HS^-/SO_4^{2-} couple:

$$SO_4^{2-} + 9H^+ + 8\acute{e} \leftrightarrow HS^- + 4H_2O(l) \qquad \log K^o = 34.0$$

$$\begin{aligned}\log K^o = 34 &= 4 \log (H_2O) - \log (HS^-) - \log (SO_4^{2-}) - 9 \log(H^+) - 8 \log (\acute{e})\\ &= 4 (-0.01) - \log (HS^-) - \log (SO_4^{2-}) + 9\,pH + 8\,p\varepsilon\end{aligned}$$

$$\text{at } pH = 7,\; p\varepsilon = (- \log (HS^-) - \log (SO_4^{2-}) - 29)/8$$

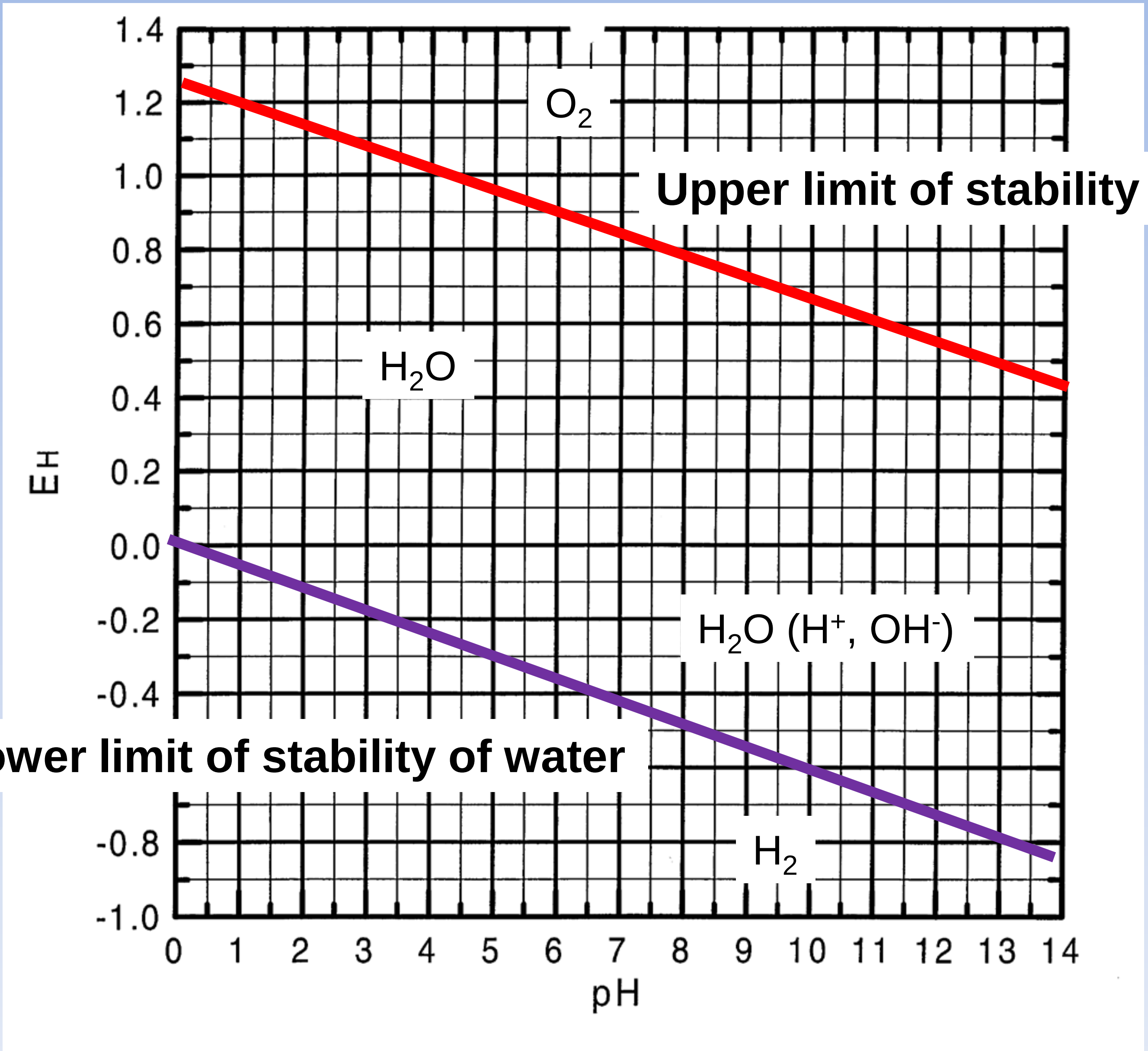
or by the S^o/SO_4^{2-} couple:

$$SO_4^{2-} + 8H^+ + 6\acute{e} \leftrightarrow S^o + 4H_2O(l) \qquad \log K^o = 36.6$$

$$\begin{aligned}\log K^o = 36.6 &= 4 \log (H_2O) - \log (S^o) - \log (SO_4^{2-}) - 8 \log(H^+) - 6 \log (\acute{e})\\ &= 4 (-0.01) - \log (S^o) - \log (SO_4^{2-}) + 8\,pH + 6\,p\varepsilon\end{aligned}$$

$$\text{at } pH = 7,\; p\varepsilon = (- \log (S^o) - \log (SO_4^{2-}) - 19.4)/6$$

Eh vs pH diagram

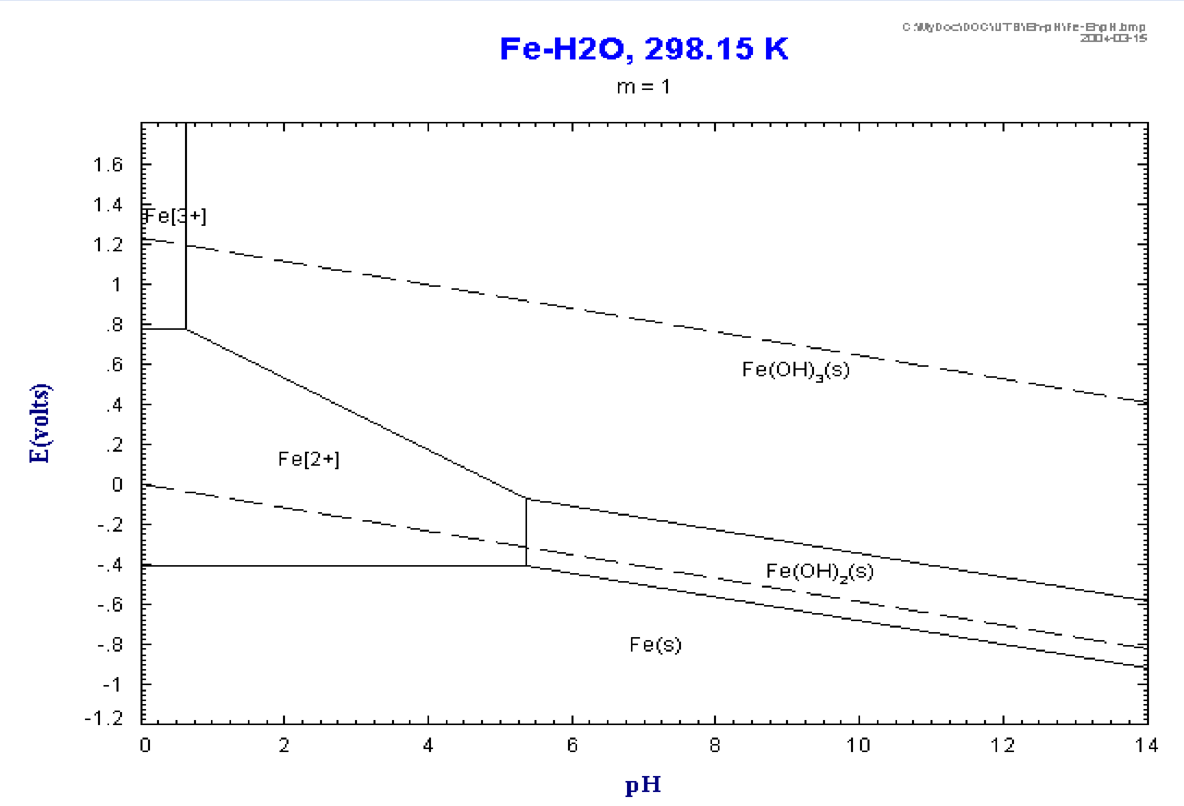


Upper limit of stability of water

Lower limit of stability of water

pε-pH and E_h-pH diagram

Taking into account hydrolysis reactions (pH-dependent), one should be able to construct pε-pH or E_h-pH diagrams for most elements and determine the predominant species in water under various environmental conditions. These diagrams are a convenient way of displaying stability relationships where redox reactions are involved.



Constructing Eh-pH diagrams: the Fe-O-H_2O system

The first thing to do is to identify the species of interest:
O_2(g), H_2(g), H_2O(l), Fe^o, Fe^{2+}, Fe^{3+}, OH^-, H^+
and a selection of solid phases
→ Fe_2O_3 and Fe_3O_4 or **$Fe(OH)_3$ and $Fe(OH)_2$**

The selection of solid phases is dependent on whether or not you wish to consider the presence of metastable phases that predominate because of kinetic constraints.

The next step is to define the boundaries between the various species based on mass-action law considerations.

The first consideration is the stability of liquid water.

- The upper stability boundary is defined by:

$\frac{1}{4} O_2(g) + H^+ + é \leftrightarrow \frac{1}{2} H_2O(l)$

$p\varepsilon = 20.77 + \frac{1}{4} \log pO_2 - pH$ or

$E_h = 1.23 + 0.015 \log pO_2 - 0.059\ pH$

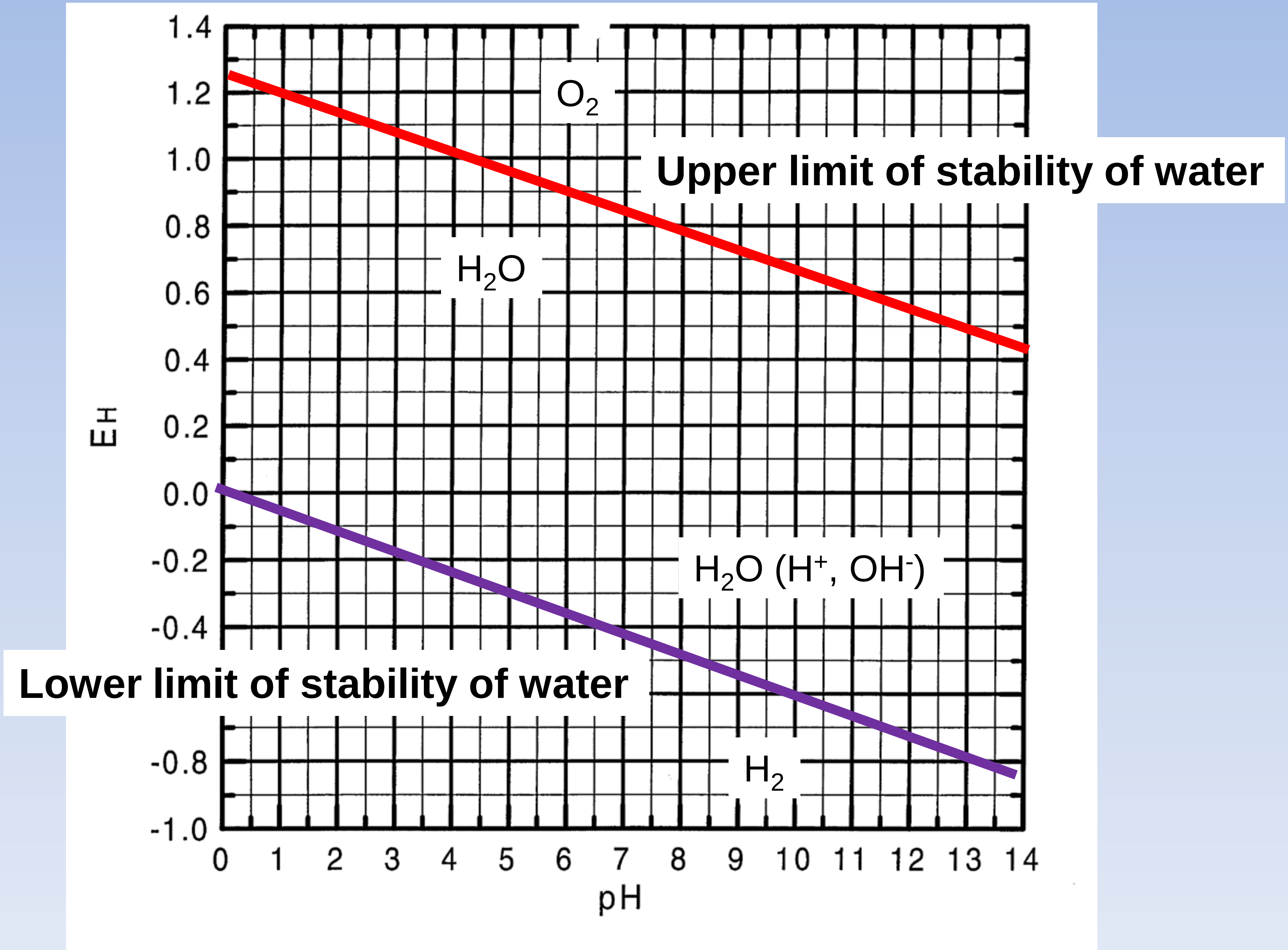
- The lower stability boundary is defined by:

$H^+ + e \leftrightarrow \frac{1}{2} H_2(g)$

$p\varepsilon = -1/2 \log pH_2 - pH$ or

$E_h = -0.0295 \log pH_2 - 0.059\ pH$

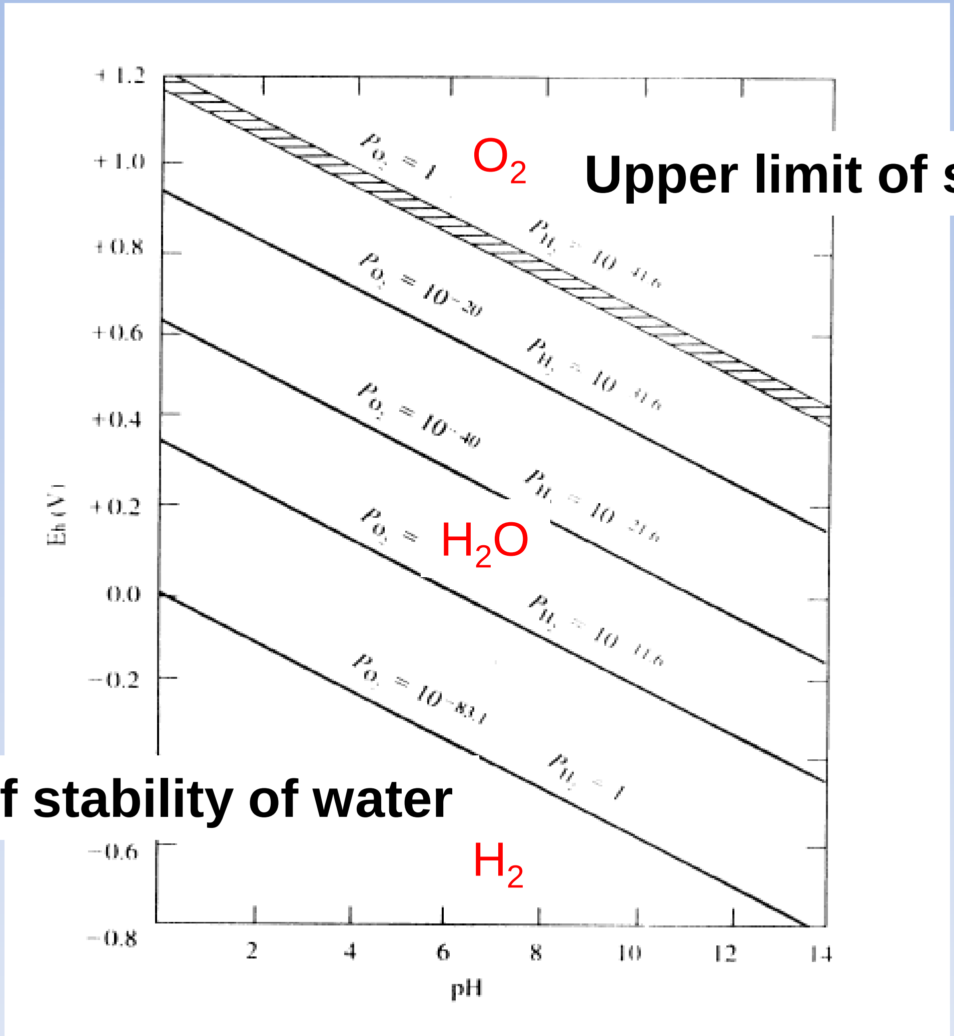
Eh vs pH diagram



Upper limit of stability of water

Lower limit of stability of water

Eh vs pH diagram



Upper limit of stability of water

Lower limit of stability of water

The Eh-pH diagram for the Fe-O-H_2O system

Let us now consider the boundary between $Fe(OH)_3$ and Fe^{3+}

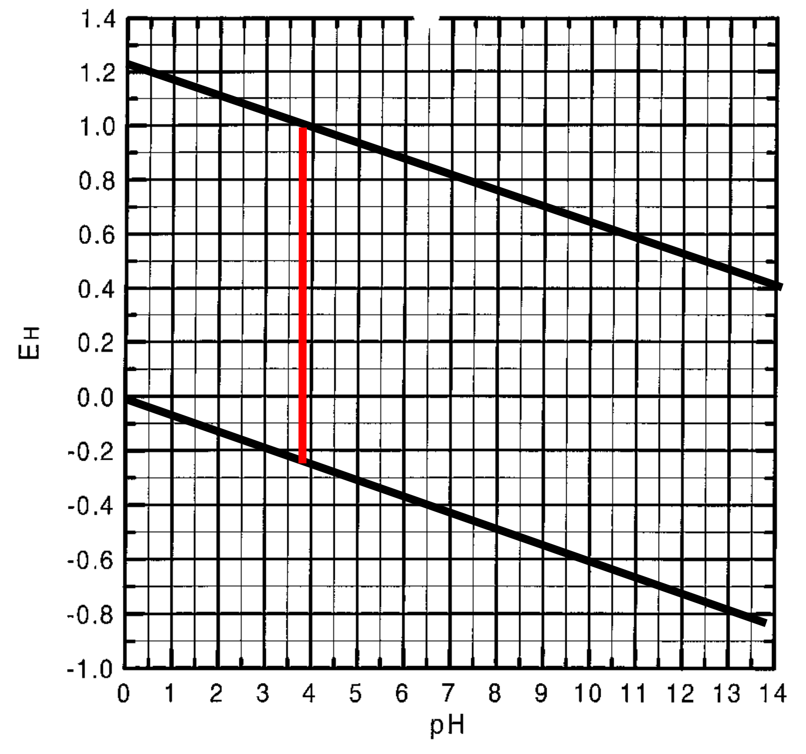
$$Fe(OH)_3 + 3H^+ \leftarrow\rightarrow Fe^{3+} + 3H_2O$$

$$K^o_{eq} = (Fe^{3+})/(H^+)^3 \quad \text{or} \quad \log K^o_{eq} = \log (Fe^{3+}) + 3\ pH$$

$$\begin{aligned} pH &= 1/3 (\log K^o_{eq} - \log (Fe^{3+})) \\ &= 1/3 (4.89 - \log (Fe^{3+})) \\ &= 3.63 \end{aligned}$$

where the value of K^o_{eq} is obtained from Gibbs free energies of the species involved in the reaction.

The limit of “solubility” is generally taken to be an activity of the dissolved species of 10^{-6} (~10^{-6} m). The choice is arbitrary but reasonable.



The Eh-pH diagram for the Fe-O-H_2O system

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$$K^o_{eq} = (Fe^{3+})/(H^+)^3 \quad \text{or} \quad \log K^o_{eq} = \log (Fe^{3+}) + 3\text{ pH}$$

$$\begin{aligned} pH &= 1/3 (\log K^o_{eq} - \log (Fe^{3+})) \\ &= 1/3 (4.89 - \log (Fe^{3+})) \\ &= 3.63 \end{aligned}$$

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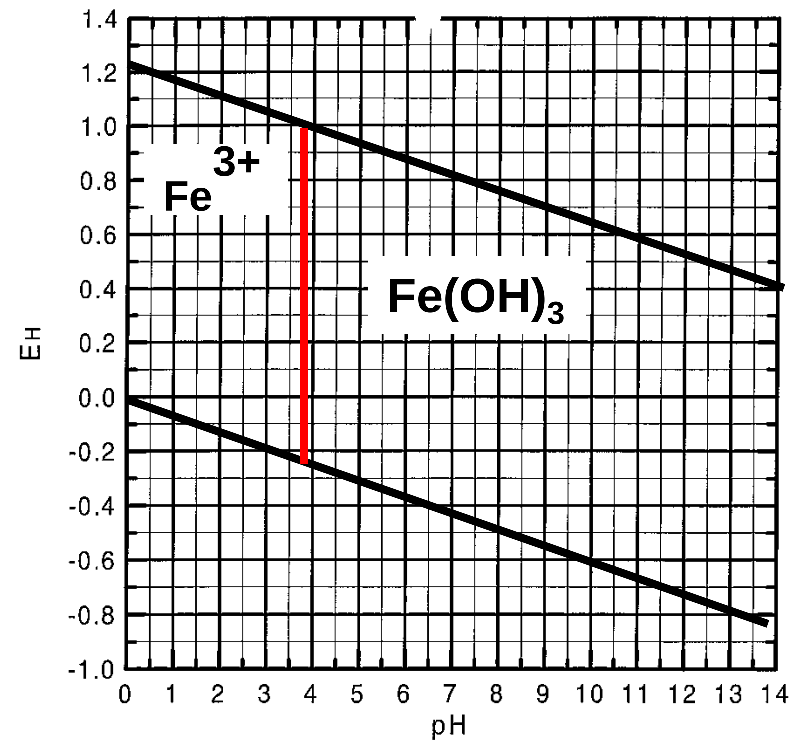


The Eh-pH diagram for the Fe-O-H_2O system

The boundary for Fe^{3+} and Fe^{2+} is given by:

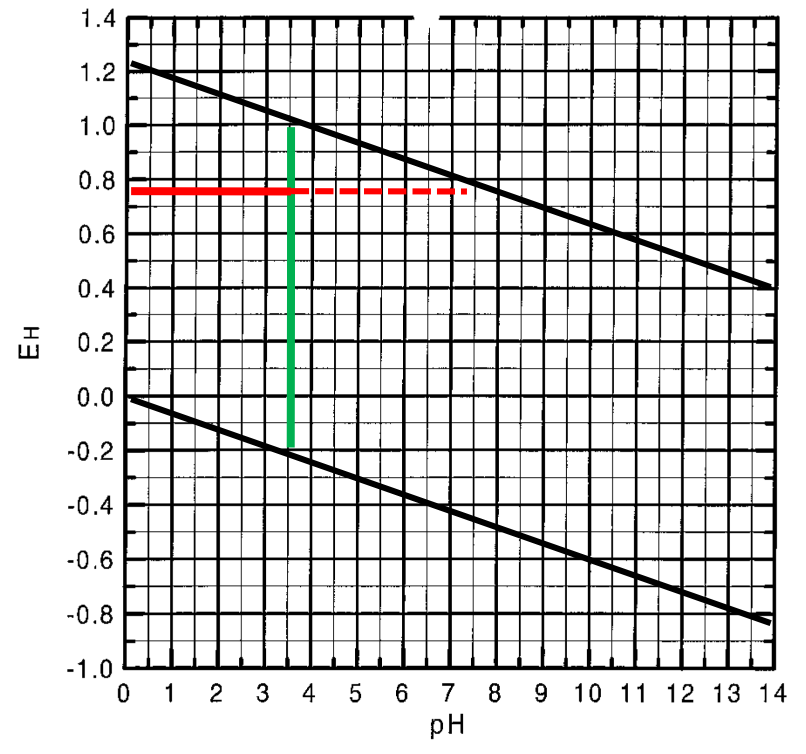
Fe^{3+} + é ←→ Fe^{2+}

$K^o_{eq} = (Fe^{2+})/((Fe^{3+})(é))$ or $\log K^o_{eq} = \log (Fe^{2+})/(Fe^{3+}) + p\varepsilon$

$$p\varepsilon = \log K^o_{eq} - \log (Fe^{2+})/(Fe^{3+})$$
$$= 13.02 - \log (Fe^{2+})/(Fe^{3+})$$

$$E_h = 0.77 – 0.059 \log (Fe^{2+})/(Fe^{3+})$$

Since the boundary is independent of pH, it must plot as a horizontal line.
To draw the boundary, however, we must assign a value to the ratio $(Fe^{2+})/(Fe^{3+})$, typically 1.



The Eh-pH diagram for the Fe-O-H_2O system

The boundary for Fe^{3+} and Fe^{2+} is given by:

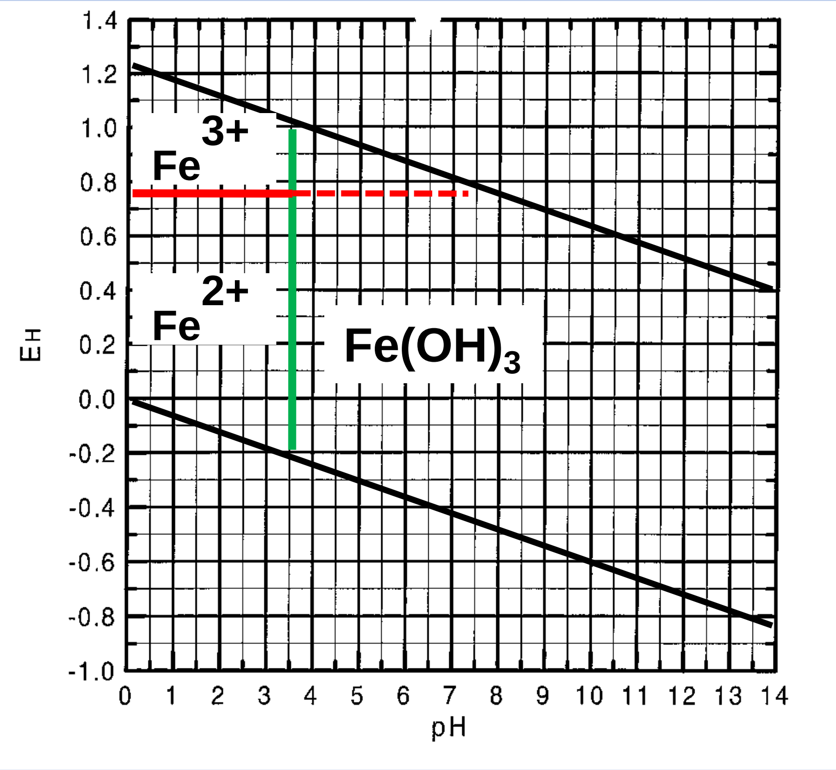
$Fe^{3+} + é \leftrightarrow Fe^{2+}$

$K^o_{eq} = (Fe^{2+})/((Fe^{3+})(é))$ or $\log K^o_{eq} = \log (Fe^{2+})/(Fe^{3+}) + p\varepsilon$

$p\varepsilon = \log K^o_{eq} - \log (Fe^{2+})/(Fe^{3+})$
$= 13.02 - \log (Fe^{2+})/(Fe^{3+})$

$E_h = 0.77 – 0.059 \log (Fe^{2+})/(Fe^{3+})$

Since the boundary is independent of pH, it must plot as a horizontal line.
To draw the boundary, however, we must assign a value to the ratio $(Fe^{2+})/(Fe^{3+})$, typically 1.



The Eh-pH diagram for the Fe-O-H_2O system

The boundary between $Fe(OH)_3$ and Fe^{2+} is given by:

$Fe(OH)_3 + 3H^+ + é \leftarrow\rightarrow Fe^{2+} + 3H_2O$

$K^o_{eq} = (Fe^{2+})/((H^+)^3\,(é))$ or

$\log K^o_{eq} = \log (Fe^{2+}) + 3\ pH + p\varepsilon$

$p\varepsilon = \log K^o_{eq} - \log (Fe^{2+}) - 3\ pH$

$= 17.9 - \log (Fe^{2+}) - 3\ pH$

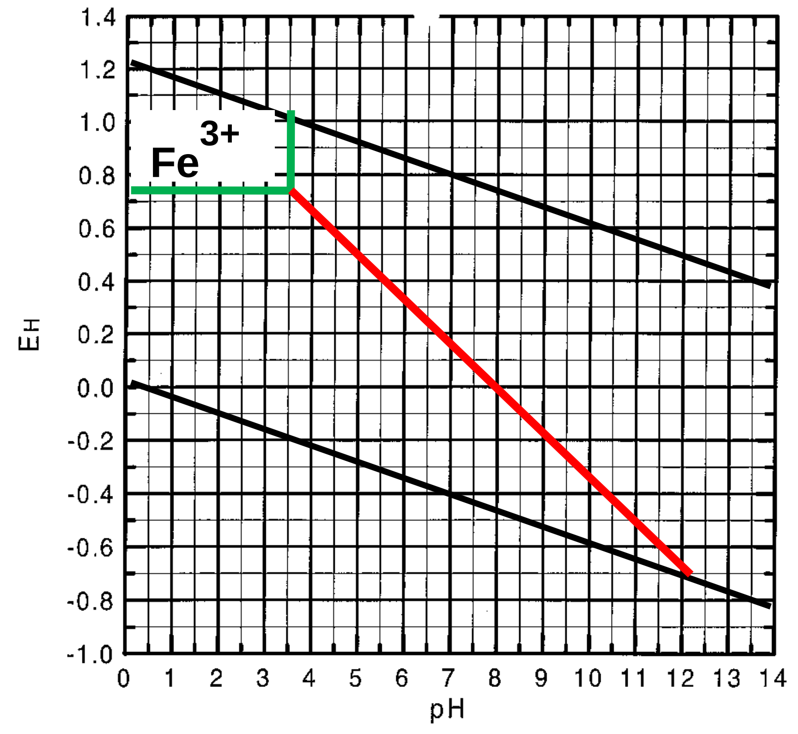
given $(Fe^{2+}) = 10^{-6}$

$p\varepsilon = 23.9 – 3pH$

$E_h = 1.06 - 0.177\ pH$

$- 0.059 \log (Fe^{2+})$

$= 1.41 - 0.177\ pH$



The Eh-pH diagram for the Fe-O-H_2O system

The boundary between $Fe(OH)_3$ and Fe^{2+} is given by:

$Fe(OH)_3 + 3H^+ + é \leftarrow\rightarrow Fe^{2+} + 3H_2O$

$K^o_{eq} = (Fe^{2+})/((H^+)^3 (é))$ or

$\log K^o_{eq} = \log (Fe^{2+}) + 3\ pH + p\varepsilon$

$p\varepsilon = \log K^o_{eq} - \log (Fe^{2+}) - 3\ pH$

$= 17.9 - \log (Fe^{2+}) - 3\ pH$

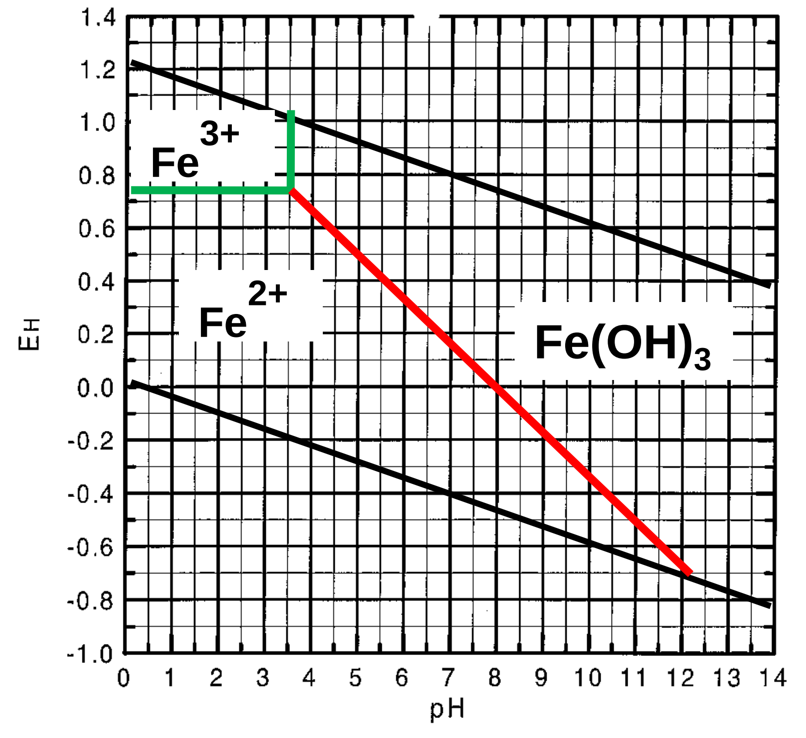
given $(Fe^{2+}) = 10^{-6}$

$p\varepsilon = 23.9 - 3pH$

$E_h = 1.06 - 0.177\ pH$

$- 0.059 \log (Fe^{2+})$

$= 1.41 - 0.177\ pH$



The Eh-pH diagram for the Fe-O-H_2O system

The boundaries involving $Fe(OH)_2$ are:

$Fe(OH)_2 + 2H^+ \leftarrow\rightarrow Fe^{2+} + 2H_2O$

$K^o_{eq} = (Fe^{2+})/(H^+)^2$,

pH = ½ (log K^o_{eq} – log (Fe^{2+})) = ½ (12.4 - log (Fe^{2+})) = 9.2

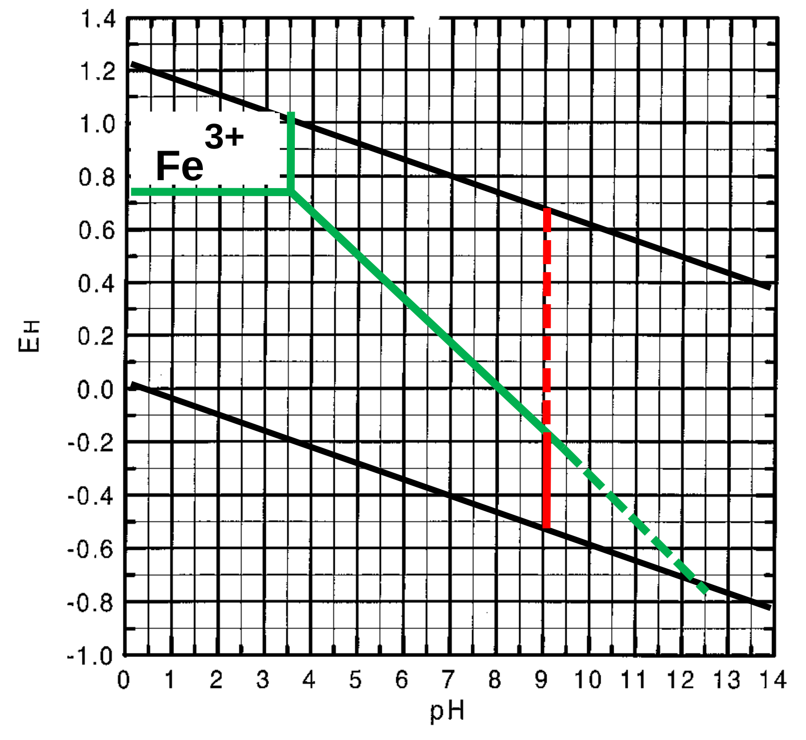
$Fe(OH)_3 + H^+ + é \leftarrow\rightarrow Fe(OH)_2 + H_2O$

$K^o_{eq} = 1/((H^+)(é))$,

pε = log K^o_{eq} – pH

= 5.53 – pH or

$E_h = 0.33 - 0.059$ pH



The Eh-pH diagram for the Fe-O-H_2O system

The boundaries involving $Fe(OH)_2$ are:

$Fe(OH)_2 + 2H^+ \leftarrow\rightarrow Fe^{2+} + 2H_2O$

$K^o_{eq} = (Fe^{2+})/(H^+)^2$,

$pH = ½ (\log K^o_{eq} – \log (Fe^{2+})) = ½ (12.4 - \log (Fe^{2+})) = 9.2$

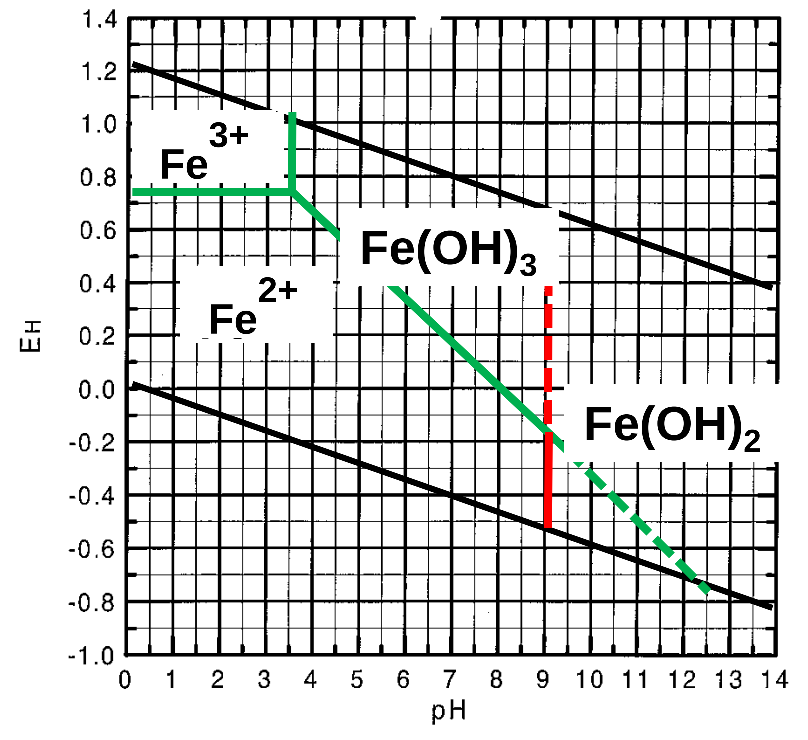
$Fe(OH)_3 + H^+ + é \leftarrow\rightarrow Fe(OH)_2 + H_2O$

$K^o_{eq} = 1/((H^+)(é))$,

$p\varepsilon = \log K^o_{eq} – pH$

$= 5.53 – pH$ or

$E_h = 0.33 – 0.059 pH$



The Eh-pH diagram for the Fe-O-H_2O system

The boundaries involving $Fe(OH)_2$ are:

$Fe(OH)_2 + 2H^+ \leftarrow\rightarrow Fe^{2+} + 2H_2O$

$K^o_{eq} = (Fe^{2+})/(H^+)^2$,

$pH = ½ (\log K^o_{eq} – \log (Fe^{2+})) = ½ (12.4 - \log (Fe^{2+})) = 9.2$

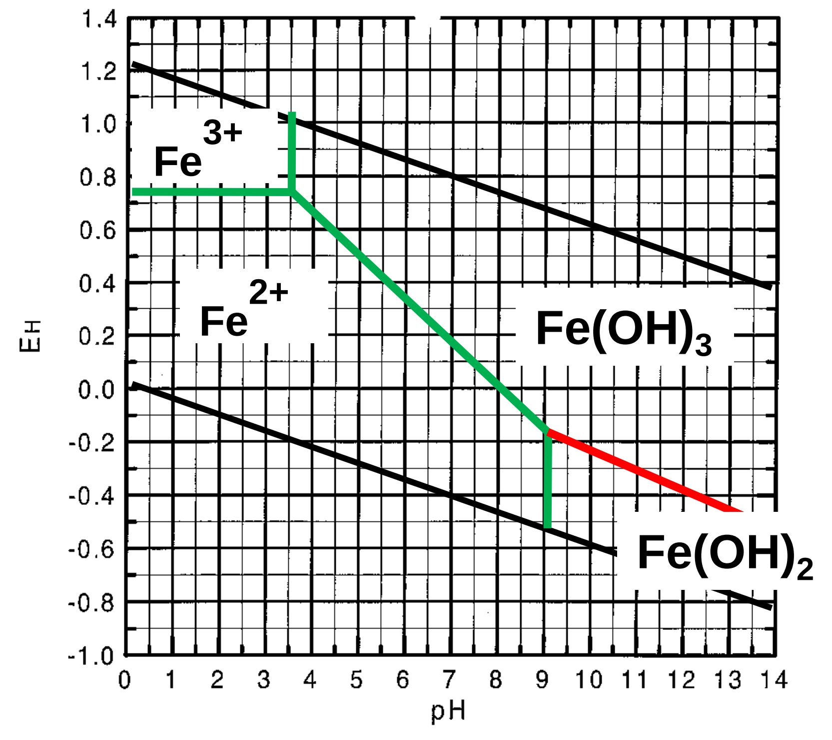
$Fe(OH)_3 + H^+ + é \leftarrow\rightarrow Fe(OH)_2 + H_2O$

$K^o_{eq} = 1/((H^+)(é))$,

$p\varepsilon = \log K^o_{eq} – pH$

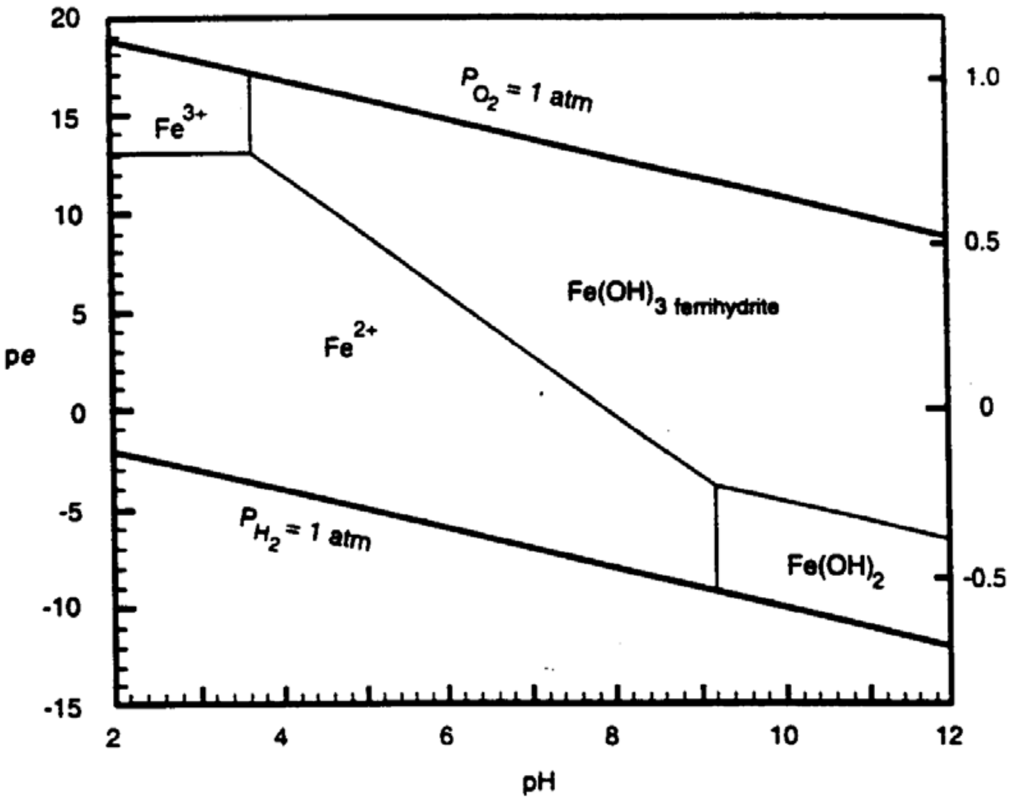
$= 5.53 – pH$ or

$E_h = 0.33 – 0.059\ pH$



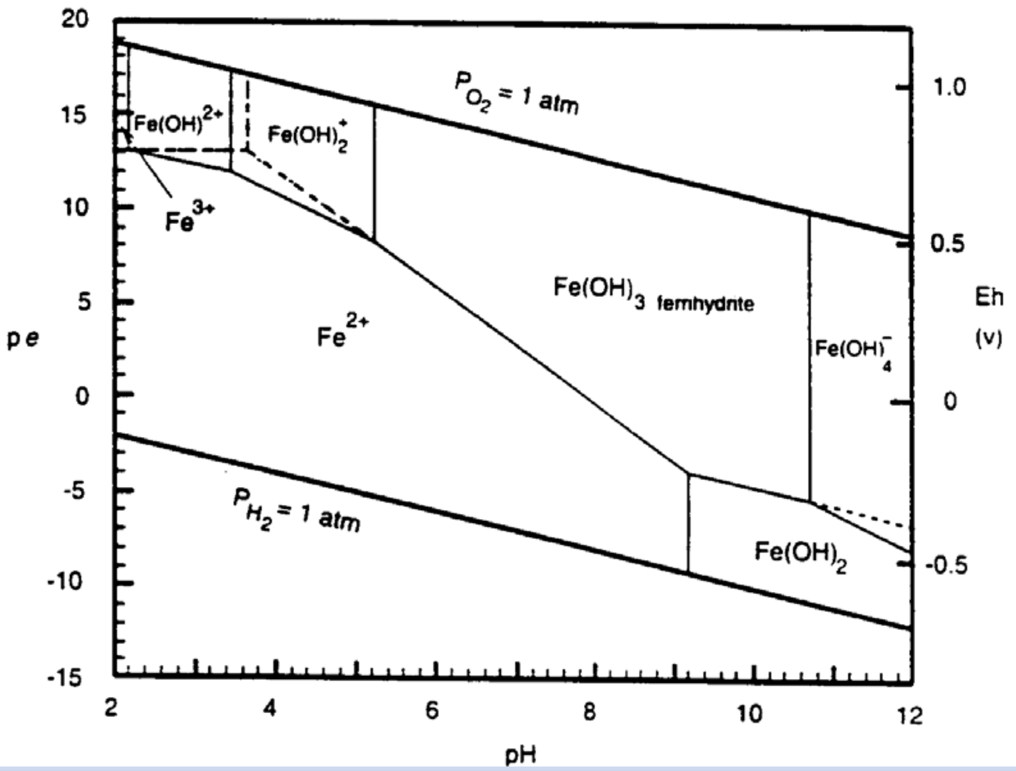
pε-pH diagram for the Fe-O-H_2O system (with ferrihydrite)

FIGURE 7-5 pe–pH diagram for the system Fe–O–H_2O at 25°C with ferrihydrite ($Fe(OH)_3$) as the ferric oxide instead of hematite and $Fe(OH)_2$ instead of magnetite. Solid-solution boundaries are drawn for an activity of dissolved Fe species of 10^{-6}.



pε-pH diagram for the Fe-O-H_2O system

FIGURE 7-6 *pe*–pH diagram for the system Fe–O–H_2O with ferrihydrite as the ferric oxide, including the hydrolyzed forms of Fe^{3+}. Dashed lines are copied from Figure 7-5. Solid-solution boundaries are drawn for an activity of dissolved Fe species of 10^{-6}.



$Fe^{3+} + H_2O \leftrightarrow Fe(OH)^{2+} + H^+$

$K_{eq} = (Fe(OH)_2^+)(H^+)/(Fe^{3+})$, $pH = -\log K_{eq} + \log ((Fe(OH)_2^+/(Fe^{3+})) = 2.19$

The other boundaries are:

$Fe(OH)^{2+} + H_2O \leftrightarrow Fe(OH)_2^+ + H^+$, $\log K_{eq} = -3.48$, pH = 3.48

$Fe(OH)_3(s) + H^+ \leftrightarrow Fe(OH)_2^+ + H_2O$, $\log K_{eq} = -0.78$, pH = 5.22 for $(Fe(OH)_2^+) = 10^{-6}$

$Fe(OH)_3(s) \leftrightarrow Fe(OH)_3^o$, $\log K_{eq} = -7.67$.

pε-pH diagram for the Fe-O-H_2O system

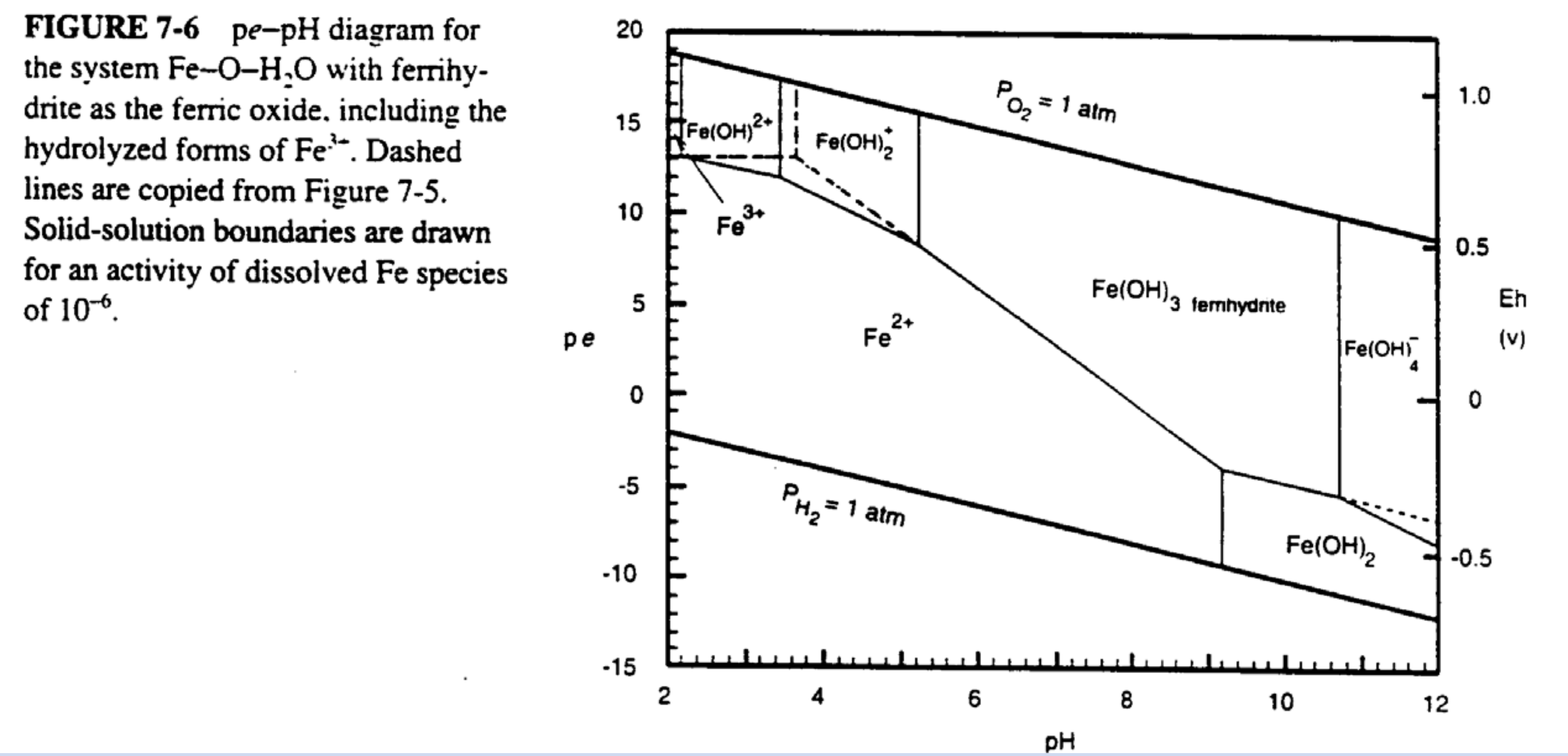


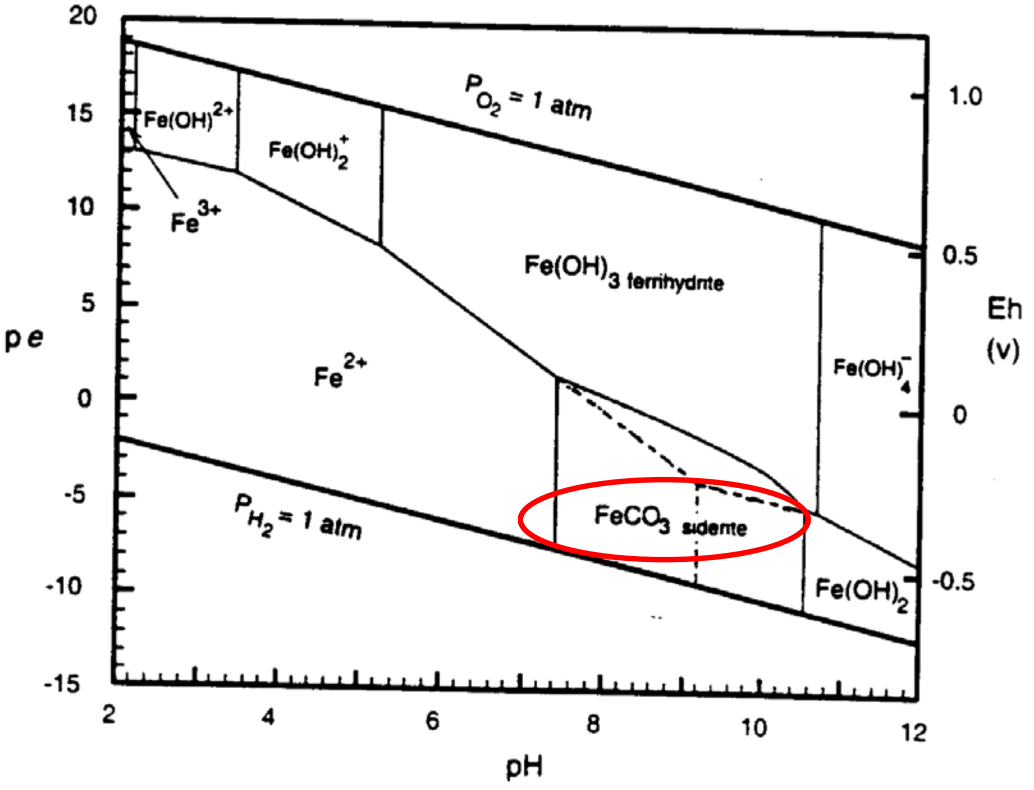
FIGURE 7-6 pe–pH diagram for the system Fe–O–H_2O with ferrihydrite as the ferric oxide, including the hydrolyzed forms of Fe^{3+}. Dashed lines are copied from Figure 7-5. Solid-solution boundaries are drawn for an activity of dissolved Fe species of 10^{-6}.

$Fe(OH)^{2+}$ + é $\leftarrow\rightarrow$ $Fe^{2+} + H_2O$, and
$Fe(OH)_2^+$ + é + $2H^+$ $\leftarrow\rightarrow$ $Fe^{2+} + 2H_2O$

$Fe(OH)_4^-$ + $2H^+$ + é $\leftarrow\rightarrow$ $Fe(OH)_2 + 2H_2O$
$pe = \log K_{eq} + \log (Fe(OH)_4^-) - 2pH$

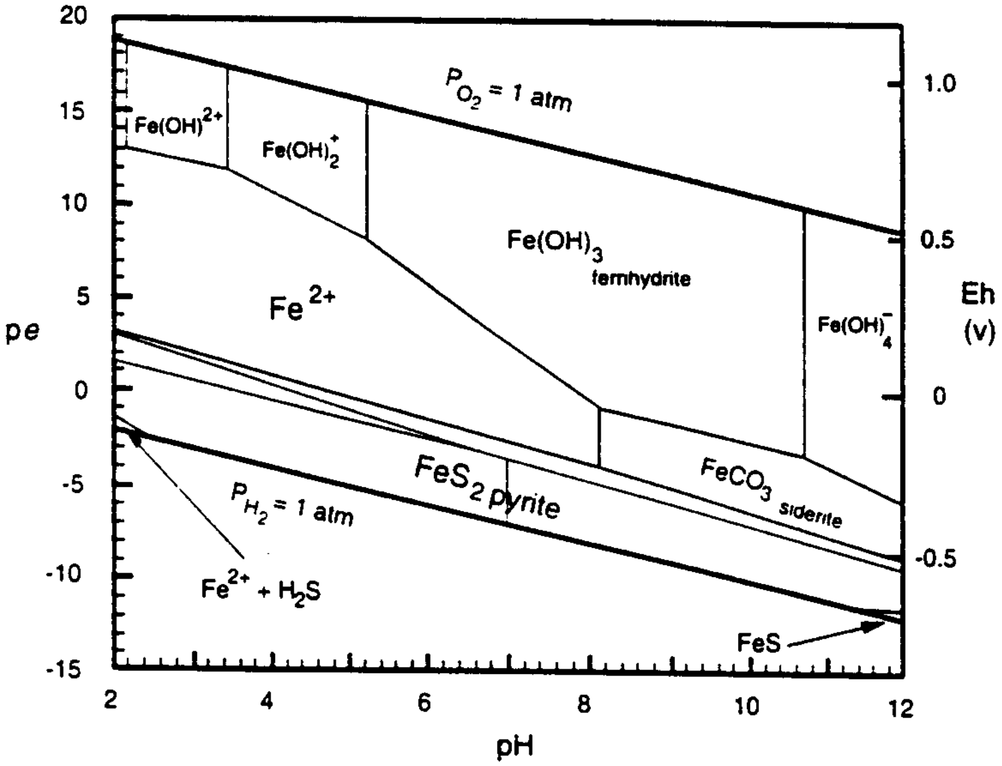
pε-pH diagram for the Fe-O-H_2O-CO_2 system

FIGURE 7-9 pe–pH diagram for the system Fe–O–H_2O–CO_2 at 25°C, considering the phases ferrihydrite, siderite, and $Fe(OH)_2$. $\Sigma CO_2 = 10^{-2}$ m. Solid–solution boundaries are drawn for an activity of dissolved Fe species of 10^{-6}.



pε-pH diagram for the Fe-O-H_2O-S-CO_2 system

FIGURE 7-14 Stability relations in the system Fe–O–H_2O–S–CO_2 at 25°C, assuming ferrihydrite as the ferric oxide phase, $\sum S = 10^{-2}$m and $P_{CO_2} = 10^{-3}$ atm. Solid–solution boundaries are drawn for an activity of dissolved Fe species of 10^{-6}. Light lines are boundaries for sulfur species from Fig. 7-11.

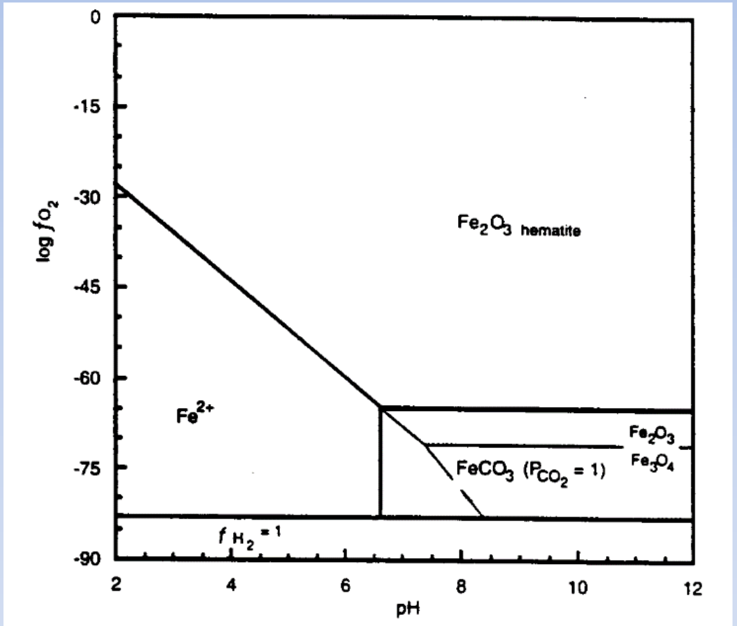


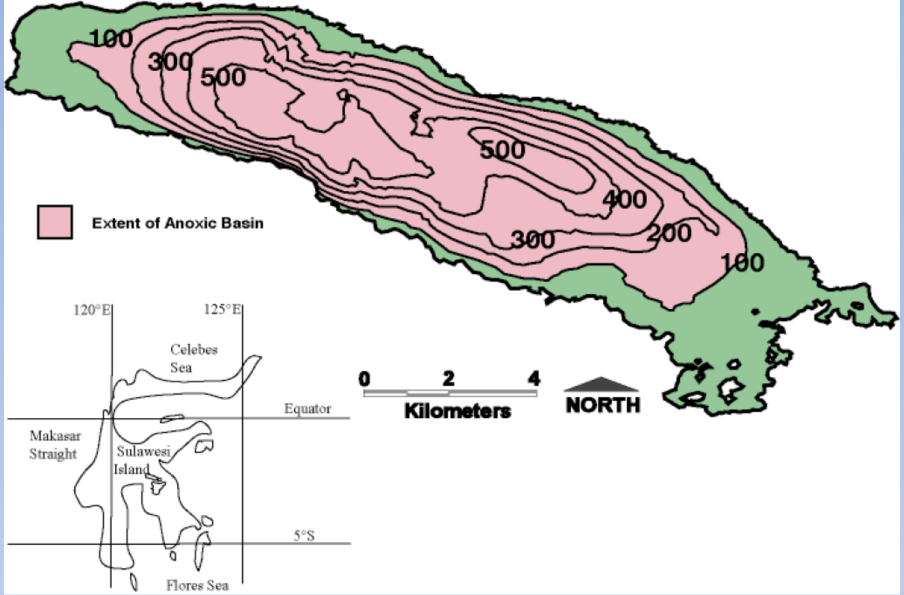
Partial pressure or fugacity-fugacity diagrams

For the Fe_2O_3-Fe_3O_4 reaction,
$3Fe_2O_3 \leftarrow\rightarrow 2Fe_3O_4 + ½ O_2$
$K_{eq} = (fO_2)^{1/2}$, log fO_2 = 2 log K_{eq} = -70
This plots as a horizontal line in both figures

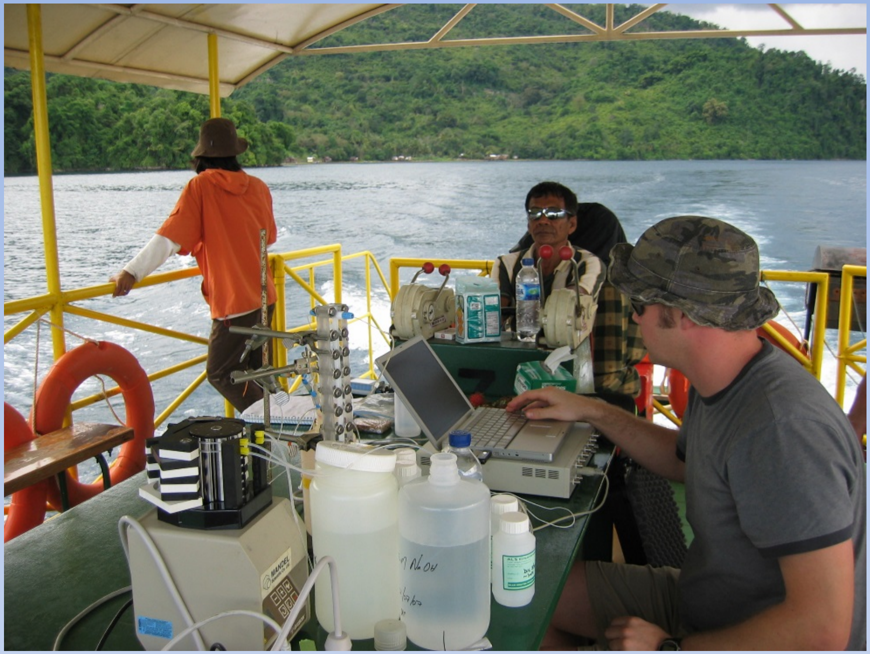
For the following reaction,
$Fe_2O_3 + 4H^+ \leftarrow\rightarrow 2Fe^{2+} + 2H_2O + ½ O_2$
$\log K_{eq} = 2 \log (Fe^{2+}) + ½ \log fO_2 + 4pH$
This plots as a line of slope –8 on the log fO_2*-pH*

$FeCO_3$-Fe^{2+}
$FeCO_3 + 2H^+ \leftarrow\rightarrow Fe^{2+} + H_2O + CO_2$
$\log K_{eq} = \log (Fe^{2+}) + \log fCO_2 + 2pH$
This plots as a vertical line on a log fO_2*-pH diagram*

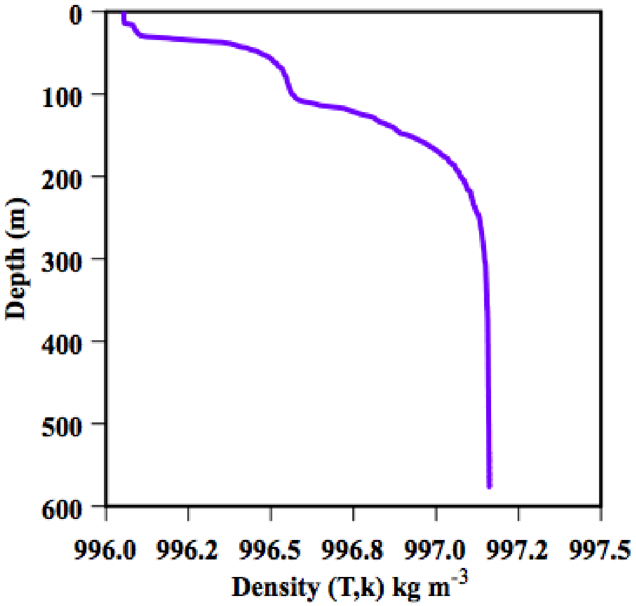


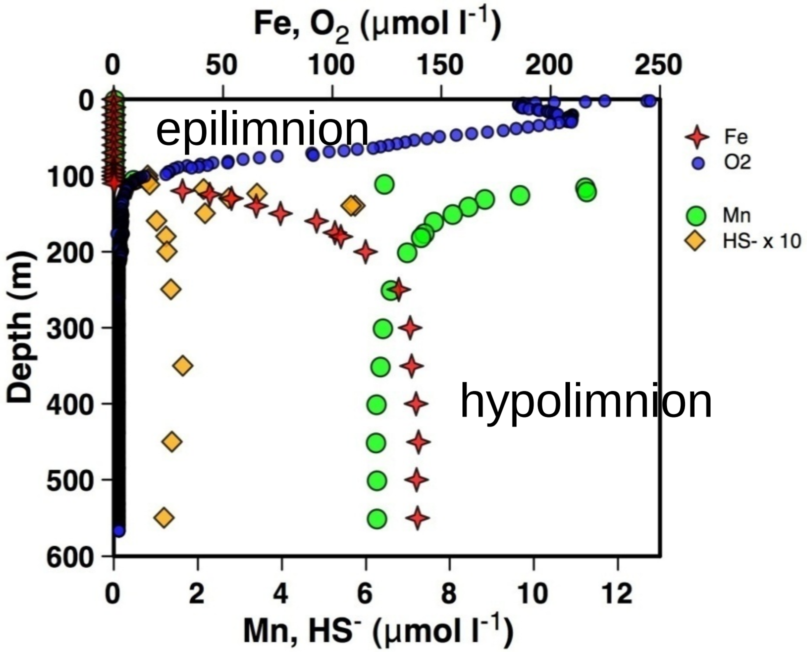


- Lake surface area -164 km^2
- Depth >590 m
- Trophic status: oligotrophic
- Seasonality in region:
  - Little temperature variation
  - Dry vs. wet seasons



Physical and Chemical stratification





- Oxic epilimnion, anoxic hypolimnion
- High (140 µmol/L) concentration of Fe(II) in the hypolimnion

pε-pH and E_h-pH diagrams

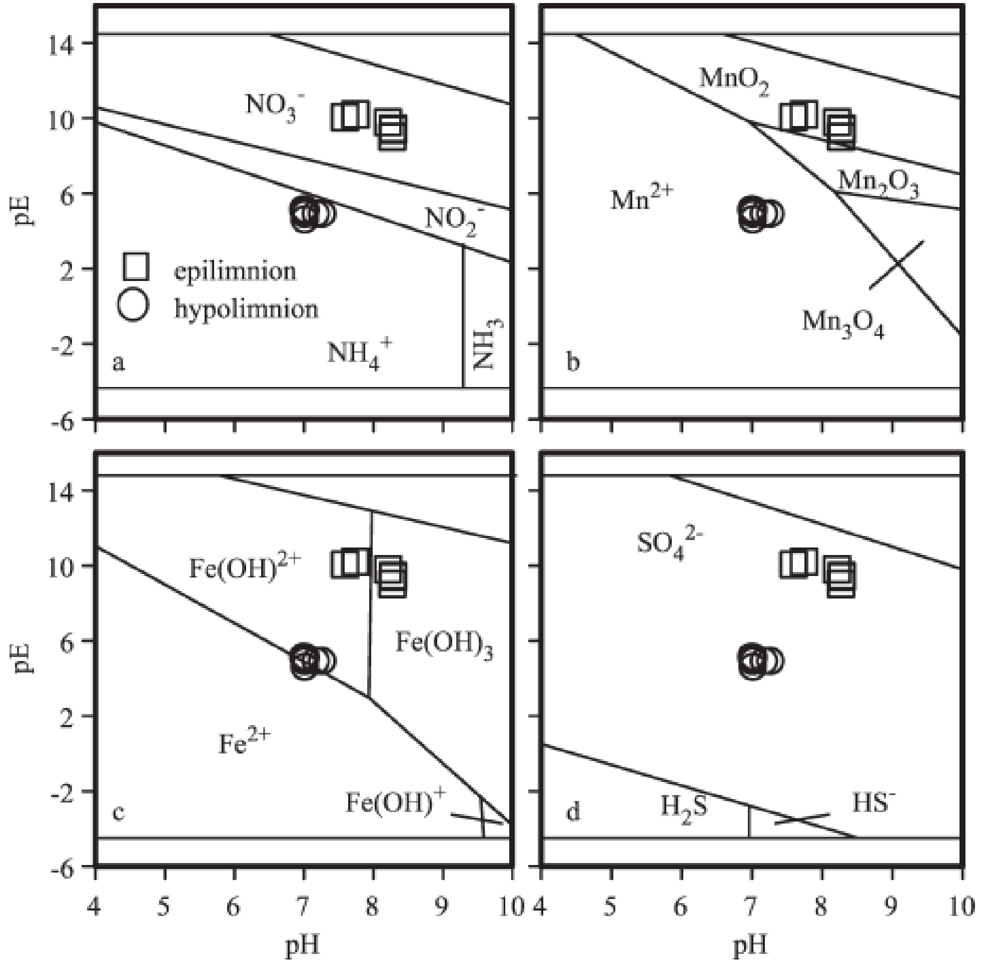
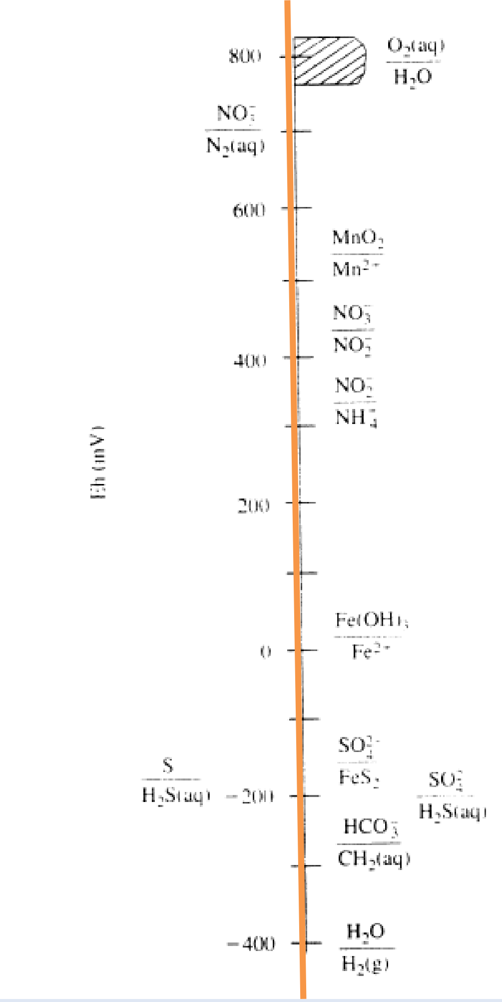


Fig. 4. pE versus pH diagrams for species of (a) nitrogen, (b) manganese, (c) iron, and (d) sulfur. Symbols are pE–pH coordinates for selected samples of Lake Matano waters. The bimodal distribution represents waters from the hypolimnion with low pE and pH values and waters from the epilimnion at relatively higher values.

From: Crowe et al. Limnol. Oceanogr. 2008

Redox conditions in natural waters

At a given pH, the oxidized species of couples having more positive Eh values can, theoretically, oxidize the reduced species of couples having a more negative Eh value and vice-versa.



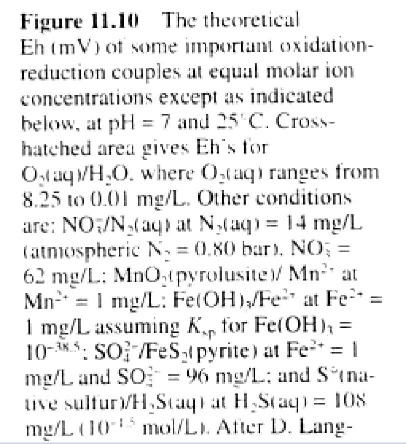


Figure 11.10 The theoretical Eh (mV) of some important oxidation-reduction couples at equal molar ion concentrations except as indicated below, at pH = 7 and 25°C. Cross-hatched area gives Eh's for $O_2(aq)/H_2O$, where $O_2(aq)$ ranges from 8.25 to 0.01 mg/L. Other conditions are: $NO_3^-/N_2(aq)$ at $N_2(aq)$ = 14 mg/L (atmospheric N_2 = 0.80 bar), NO_3^- = 62 mg/L; MnO_2(pyrolusite)/ Mn^{2+} at Mn^{2+} = 1 mg/L; $Fe(OH)_3/Fe^{2+}$ at Fe^{2+} = 1 mg/L assuming K_{sp} for $Fe(OH)_3 = 10^{-38.5}$; SO_4^{2-}/FeS_2(pyrite) at Fe^{2+} = 1 mg/L and SO_4^{2-} = 96 mg/L; and S°(native sulfur)/$H_2S(aq)$ at $H_2S(aq)$ = 108 mg/L ($10^{-1.5}$ mol/L). After D. Lang-

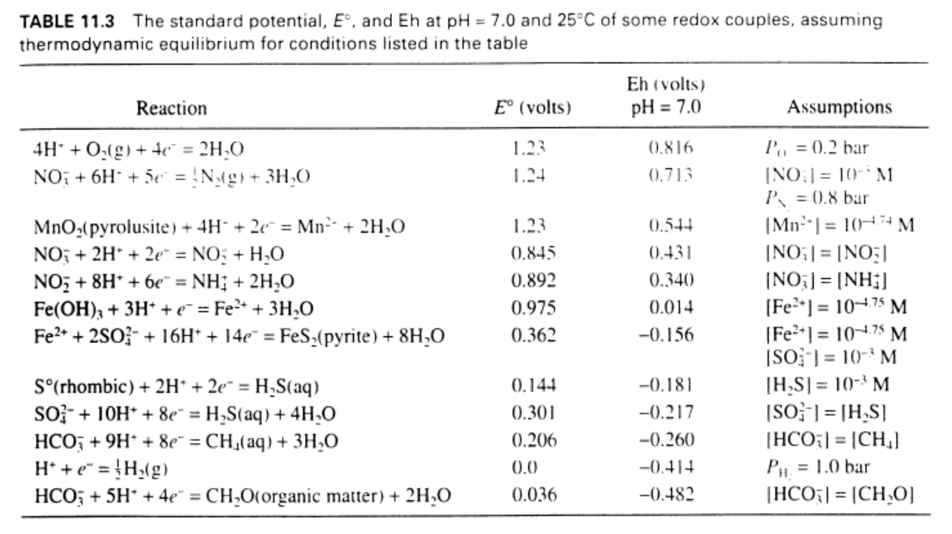


TABLE 11.3 The standard potential, E°, and Eh at pH = 7.0 and 25°C of some redox couples, assuming thermodynamic equilibrium for conditions listed in the table

Reaction	E° (volts)	Eh (volts) pH = 7.0	Assumptions
$4H^+ + O_2(g) + 4e^- = 2H_2O$	1.23	0.816	$P_{O_2} = 0.2$ bar
$NO_3^- + 6H^+ + 5e^- = \frac{1}{2}N_2(g) + 3H_2O$	1.24	0.713	$[NO_3^-] = 10^{-3}$ M $P_{N_2} = 0.8$ bar
MnO_2(pyrolusite) $+ 4H^+ + 2e^- = Mn^{2+} + 2H_2O$	1.23	0.544	$[Mn^{2+}] = 10^{-4.74}$ M
$NO_3^- + 2H^+ + 2e^- = NO_2^- + H_2O$	0.845	0.431	$[NO_3^-] = [NO_2^-]$
$NO_2^- + 8H^+ + 6e^- = NH_4^+ + 2H_2O$	0.892	0.340	$[NO_3^-] = [NH_4^+]$
$Fe(OH)_3 + 3H^+ + e^- = Fe^{2+} + 3H_2O$	0.975	0.014	$[Fe^{2+}] = 10^{-4.75}$ M
$Fe^{2+} + 2SO_4^{2-} + 16H^+ + 14e^- = FeS_2$(pyrite) $+ 8H_2O$	0.362	−0.156	$[Fe^{2+}] = 10^{-4.75}$ M $[SO_4^{2-}] = 10^{-3}$ M
S°(rhombic) $+ 2H^+ + 2e^- = H_2S(aq)$	0.144	−0.181	$[H_2S] = 10^{-3}$ M
$SO_4^{2-} + 10H^+ + 8e^- = H_2S(aq) + 4H_2O$	0.301	−0.217	$[SO_4^{2-}] = [H_2S]$
$HCO_3^- + 9H^+ + 8e^- = CH_4(aq) + 3H_2O$	0.206	−0.260	$[HCO_3^-] = [CH_4]$
$H^+ + e^- = \frac{1}{2}H_2(g)$	0.0	−0.414	$P_{H_2} = 1.0$ bar
$HCO_3^- + 5H^+ + 4e^- = CH_2O$(organic matter) $+ 2H_2O$	0.036	−0.482	$[HCO_3^-] = [CH_2O]$

Redox conditions in natural waters

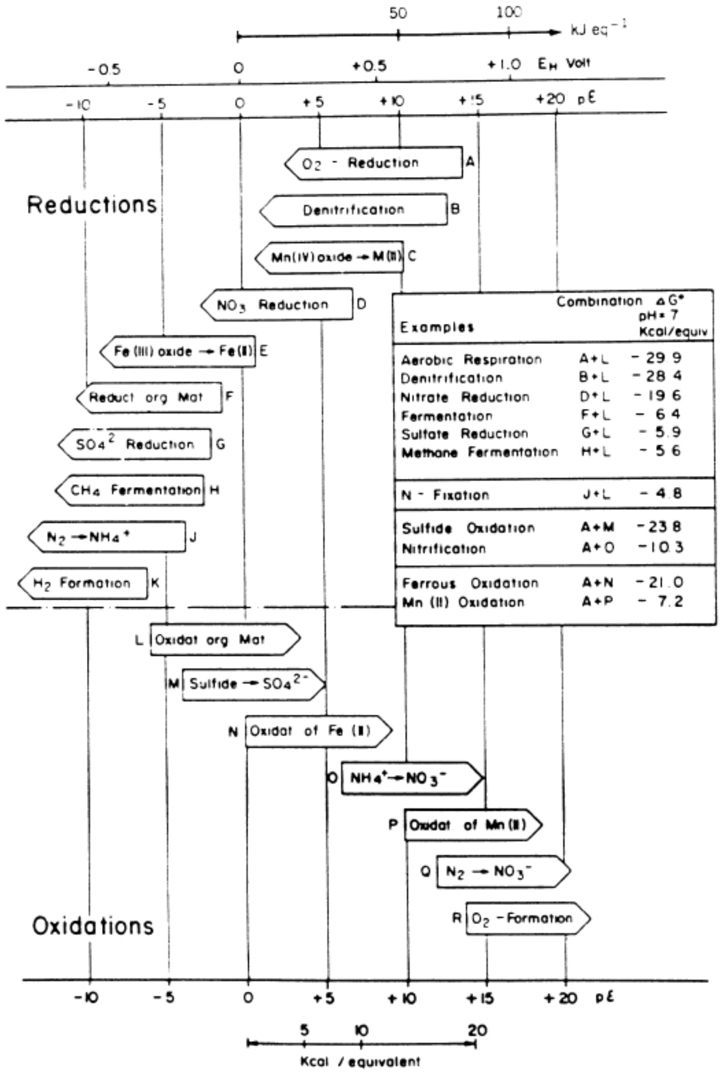


Figure 8.14. Sequence of microbially mediated redox processes. The letters refer to the reactions given in Table 8.7.

Air contains 286 mg/L of O_2 at 25^{o}C (~21% by volume). At saturation with atmospheric oxygen and 1 bar total pressure, water holds only 8.25 mg/L of dissolved oxygen (2.58×10^{-4} mol/L O_2) at 25^{o}C. If we only consider organic matter as the potential reductant, it only takes 3.1 mg/L of dissolved organic carbon to consume the 8.25 mg/L of dissolved oxygen.

The diffusion coefficient of O_2 is about 2.05×10^{-1} cm^2/s in air but only on the order of 10^{-5} cm^2/s in water, nearly four orders of magnitude slower.

Redox conditions in natural waters

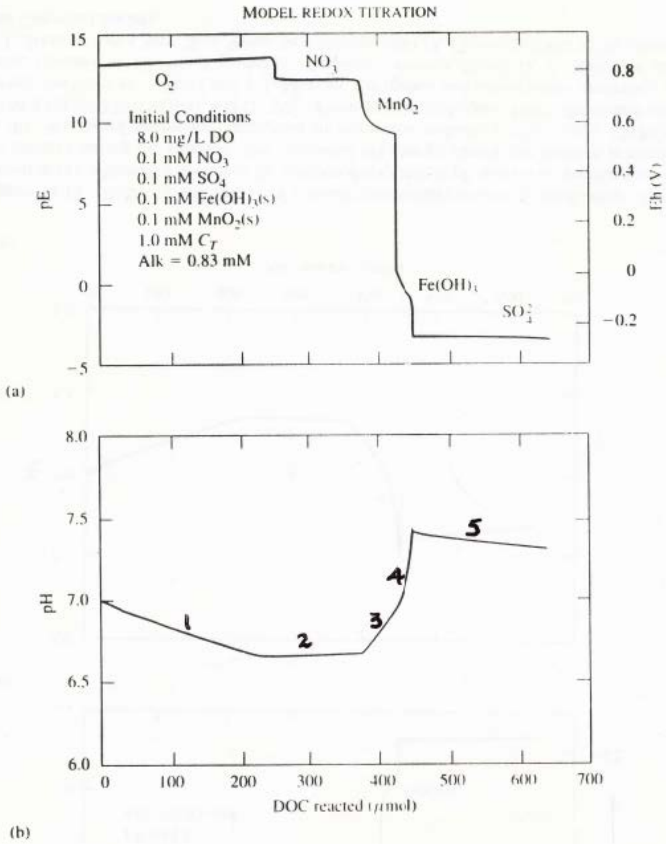


Figure 11.12 Redox titration curve of a model groundwater system of initial composition shown in **(a)**, which also describes the computed response in pE and Eh as specific species are reduced during the titration. The computed pH change during the titration is shown in **(b)**. Numbered segments correspond to sequential reduction: (1) O_2(aq), (2) NO_3^-, (3) MnO_2(s), (4) $Fe(OH)_3$(s), and (5) SO_4^{2-}. From Scott and Morgan (1990). Reprinted with permission from M. J. Scott and J. J. Morgan. Energetics and conservative properties of redox systems. In *Chemical modeling of aqueous systems II*, ed. D. C. Melchior and R. L. Bassett. Am. Chem. Soc. Symp. Ser. 416, pp. 368–78. Copyright 1990 by the American Chemical Society.

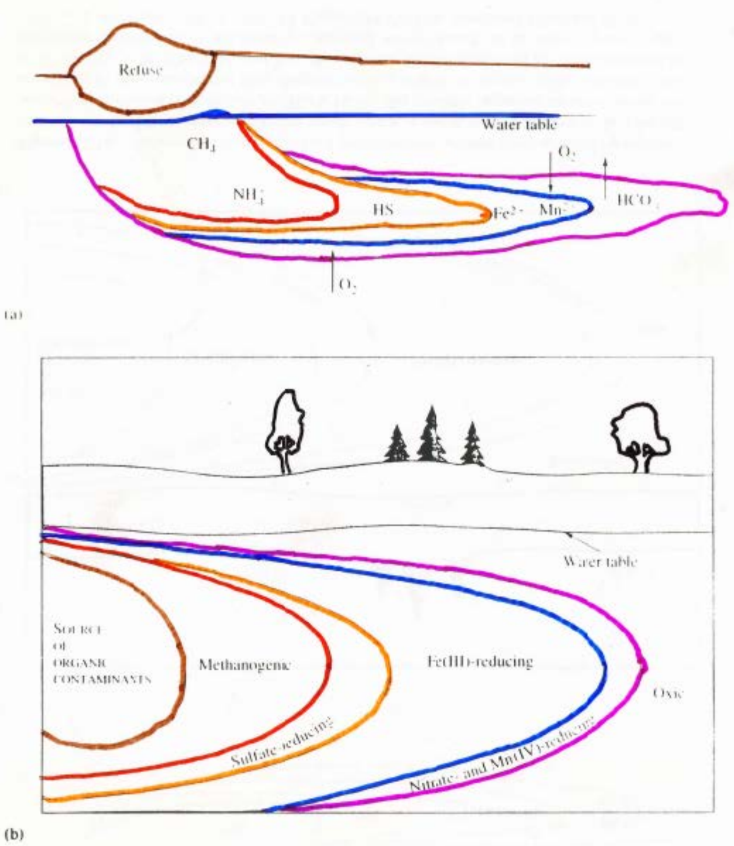


Figure 11.16 Schematic cross-sections of groundwater systems contaminated by organic-rich wastes. **(a)** Development of redox zones down gradient from a landfill in the groundwater flow direction (Baedecker and Back 1979). **(b)** Possible sequence of redox zones encountered in the groundwater flow direction from a source of organic contamination. After D. R. Lovley, F. H. Chapelle, and J. C. Woodward. Use of dissolved H_2 concentrations to determine distribution of microbially catalyzed redox reactions in anoxic groundwater. *Envir. Sci. & Technol.* 28(7):1205–10. Copyright 1994 by American Chemical Society.

Redox conditions in natural waters

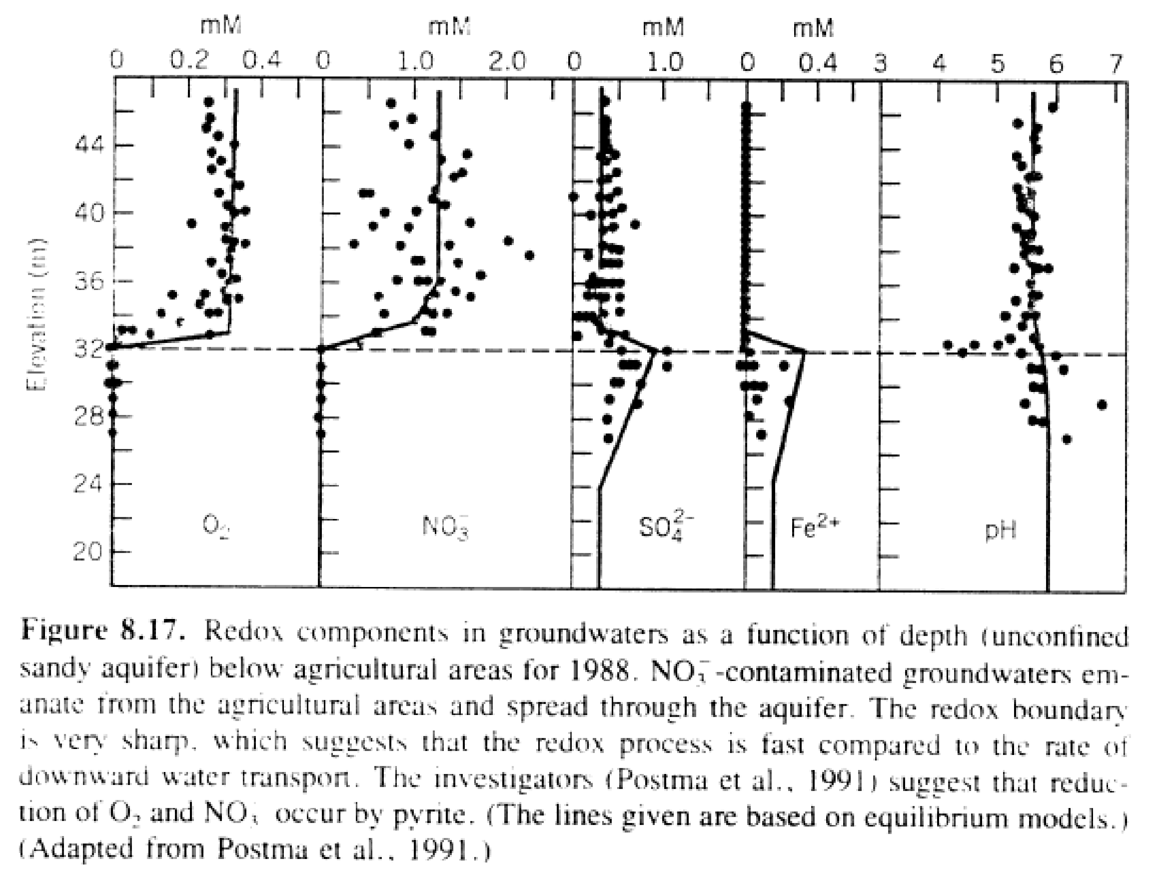


Figure 8.17. Redox components in groundwaters as a function of depth (unconfined sandy aquifer) below agricultural areas for 1988. NO_3^--contaminated groundwaters emanate from the agricultural areas and spread through the aquifer. The redox boundary is very sharp, which suggests that the redox process is fast compared to the rate of downward water transport. The investigators (Postma et al., 1991) suggest that reduction of O_2 and NO_3^- occur by pyrite. (The lines given are based on equilibrium models.) (Adapted from Postma et al., 1991.)

Redox conditions in natural waters

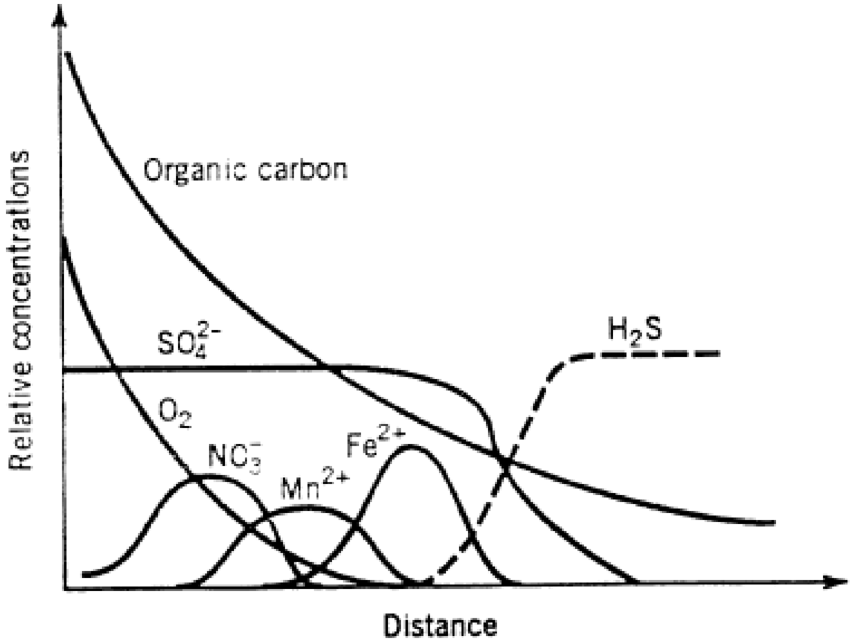


Figure 8.19. Estimation of the variation in concentration of redox species during the flow path of an organic contaminant plume.