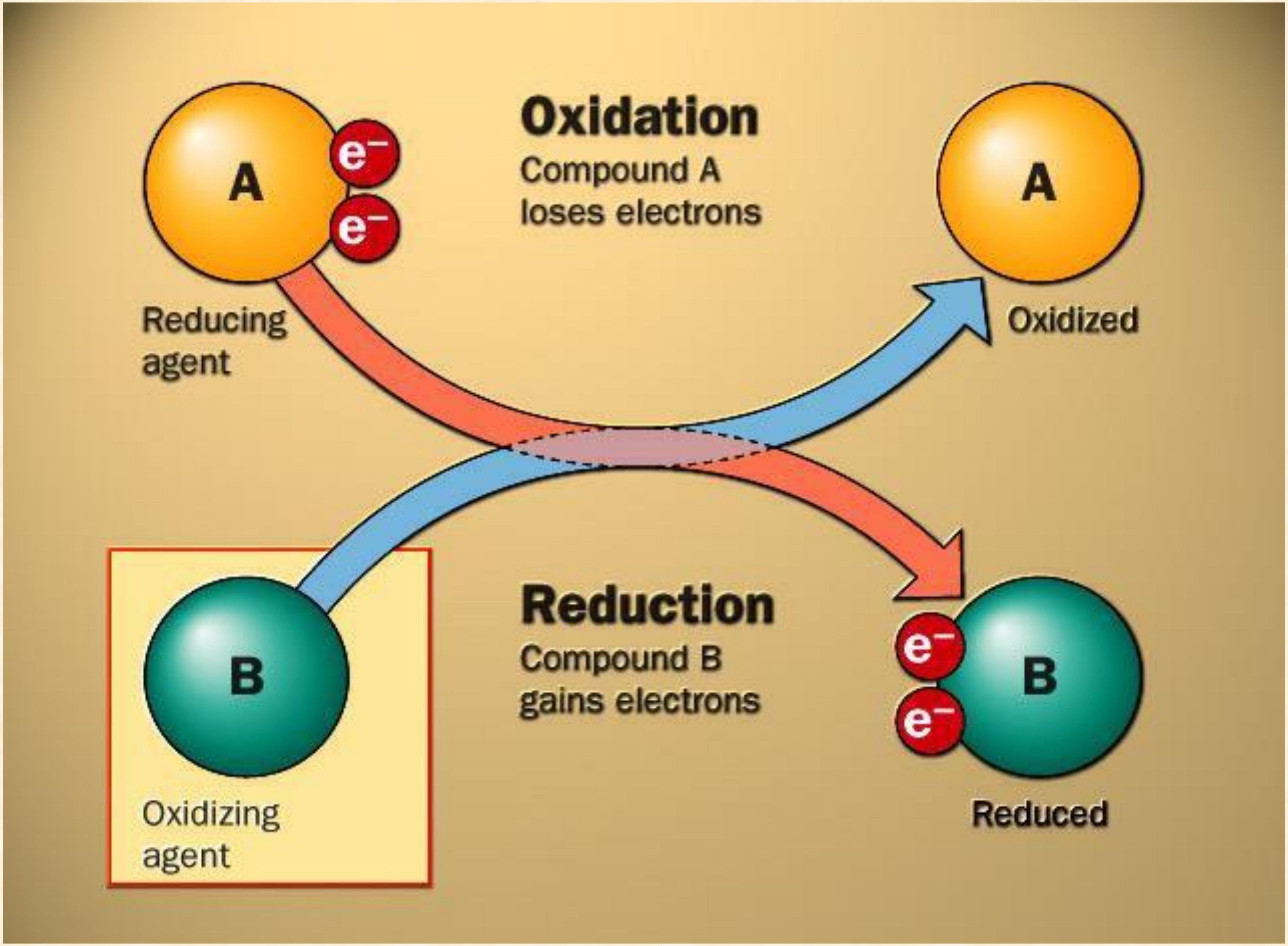
Chapter 4: Oxidation – Reduction Reactions



Oxidation – Reduction Reactions involve the gain and loss of electrons. The species involved in these reactions may be atoms, molecules,or ions.

Cation: a positively charged ion. (More protons than electrons.)

Anion: a negatively charged ion. (More electrons than protons.)

Oxidation: the loss of electrons

Reduction: the gain of electrons

Reducing agent: an electron donor (it loses electrons and is oxidized.)

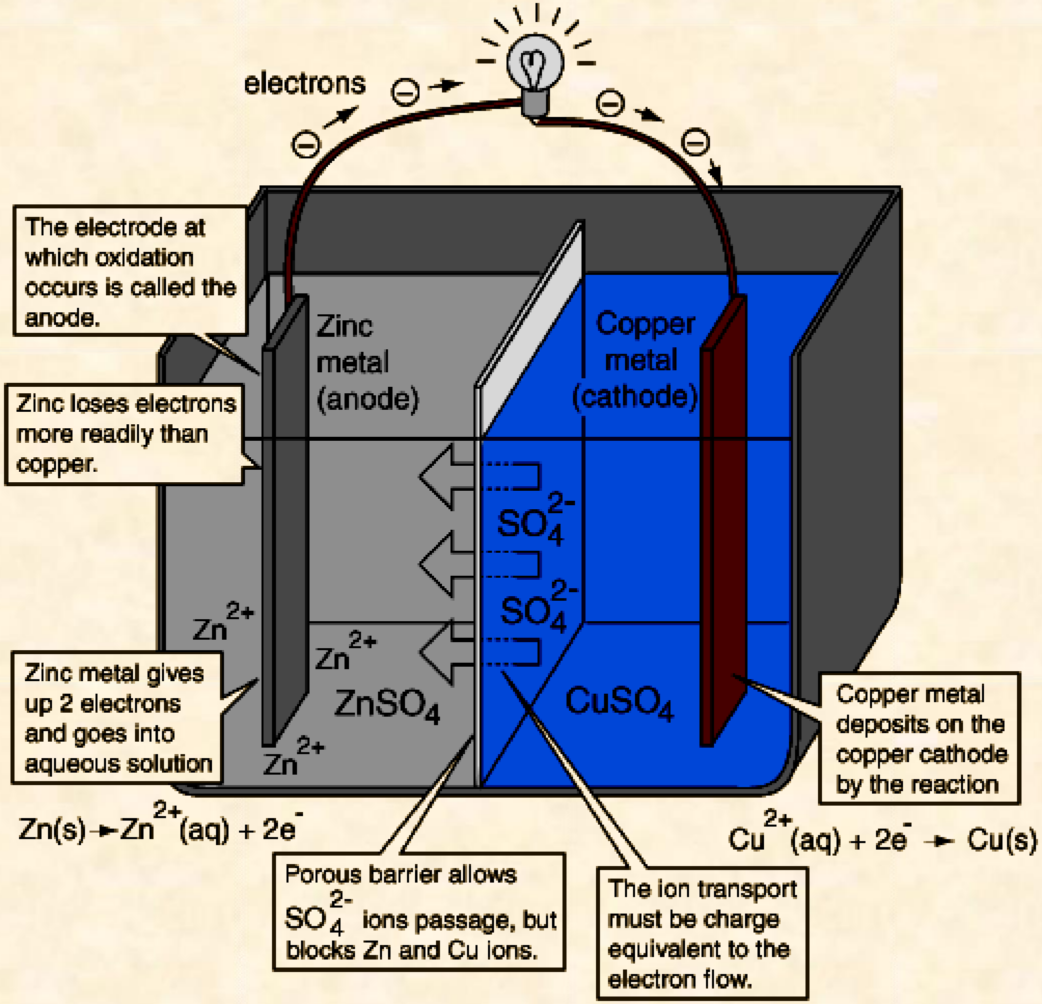
Oxidizing agent: an electron acceptor (it gains electrons and is reduced.)

Electrochemical Cell

$Zn + Cu^{2+} \leftrightarrow Zn^{2+} + Cu$

Zn more readily loses electrons than copper, therefore, it is *oxidized* and acts as a *reducing agent*.

Cu is3*reduced* and acts as an *oxidizing agent*.



The electrode at which oxidation occurs is called the anode.

Zinc loses electrons more readily than copper.

Zinc metal gives up 2 electrons and goes into aqueous solution

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

Porous barrier allows SO_4^{2-} ions passage, but blocks Zn and Cu ions.

The ion transport must be charge equivalent to the electron flow.

Copper metal deposits on the copper cathode by the reaction

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

Electromotive series: list of metals whose order indicates the relative tendency to be oxidized, or to give up electrons. Consider Table 4-1.

Table 4-1: Oxidation – Reduction Reactions Listed in an electromotive series.

Reaction	**ΔG_R (kJ / mol)**
$Zn + Fe^{2+} \leftrightarrow Zn^{2+} + Fe$	-68.4
$Fe + Cu^{2+} \leftrightarrow Fe^{2+} + Cu$	-144.4
$Cu + 2Ag^{+} \leftrightarrow Cu^{2+} + 2Ag$	-88.7

Which is the reducing agent and which is the oxidizing agent? What would happen if we combined Zn & Ag?

Take some time to look over *Table 4-2*, this electromotive series will be used often in this chapter.

***Remember these half reactions are listed in the order of decreasing strengths as reducing agents. This means the one higher up on the list will be oxidized and its half reaction on the table reversed.*

Oxidizing agent		Reducing agent	Standard electrode potential, V
Li^+	$+1e^-$ →	Li	−3.045
Na^+	$+1e^-$ →	Na	−2.714
Pu^{3+}	$+3e^-$ →	Pu	−2.07
Th^{4+}	$+4e^-$ →	Th	−1.90
Np^{3+}	$+3e^-$ →	Np	−1.86
Al^{3+}	$+3e^-$ →	Al	−1.66
U^{4+}	$+4e^-$ →	U	−1.38
Mn^{2+}	$+2e^-$ →	Mn	−1.18
V^{3+}	$+3e^-$ →	V	−0.87
Zn^{2+}	$+2e^-$ →	Zn	−0.763
S	$+2e^-$ →	S^{2-}	−0.44
Fe^{2+}	$+2e^-$ →	Fe	−0.41
Cd^{2+}	$+2e^-$ →	Cd	−0.403
Co^{2+}	$+2e^-$ →	Co	−0.277
Ni^{2+}	$+2e^-$ →	Ni	−0.250
Sn^{2+}	$+2e^-$ →	Sn	−0.140
Pb^{2+}	$+2e^-$ →	Pb	−0.126
$2H^+$	$+2e^-$ →	H_2	0.00
Ti^{4+}	$+1e^-$ →	Ti^{3+}	0.04
Sn^{4+}	$+2e^-$ →	Sn^{2+}	0.15
Cu^{2+}	$+2e^-$ →	Cu	0.337
Cu^+	$+1e^-$ →	Cu	0.521
Se	$+2e^-$ →	Se^{2-}	0.67
Fe^{3+}	$+1e^-$ →	Fe^{2+}	0.771
Ag^+	$+1e^-$ →	Ag	0.799
Pu^{4+}	$+1e^-$ →	Pu^{3+}	0.97
Au^{3+}	$+3e^-$ →	Au	1.50
Co^{3+}	$+1e^-$ →	Co^{2+}	1.82

Electromotive Force (*emf*): the maximum potential difference between two electrodes of a galvanic or voltaic cell. In figure 4-1, it is the voltage generated by the electrons flowing from the zinc bar to the copper bar.

Standard *emf* (E^o): The voltage generated under ideal conditions at a concentration of 1M.

emf is related to free energy of an oxidation reduction reaction by:

$$\Delta G_R = -nFE$$

Where ΔG_R is the free energy for the reaction, E is the corresponding electromotive force, n is the number of electrons transferred in the reaction, and *F* is Faraday’s constant (96.42 kJ / volt · gram equivalent).

Example 4-1:Calculate the standard *emf* (E^o) for the oxidation – reduction reaction in figure 4-1.

In the standard state $[Zn^{2+}] = [Cu^{2+}] = 1M$, $P = 1atm$, and $T = 25°C$.

$$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$$

$$\Delta G_R = [(-147.3) + (0.00)] - [(0.00) + (65.5)] = -212.8 \text{ kJ / mol}$$

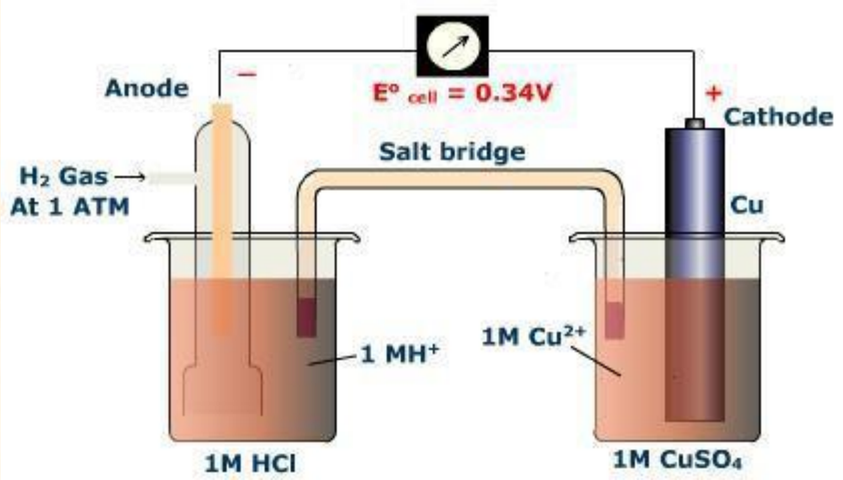
$$E° = -\Delta G_R / nF = -(-212.8) / (2)(96.42) = 1.10V$$

n = 2 because there were 2 electrons transferred in the reaction.

This problem can also be solved using the electromotive series by adding half reactions:

$$\begin{array}{ll} \mathrm{Zn} \rightarrow \mathrm{Zn}^{2+} + 2e^- & E = 0.763 \\ \underline{\mathrm{Cu}^{2+} + 2e^- \rightarrow \mathrm{Cu}\qquad\qquad} & \underline{E = 0.337\ }\ E \\ \mathrm{Zn} + \mathrm{Cu}^{2+} \rightarrow \mathrm{Zn}^{2+} + \mathrm{Cu} & = 1.100\mathrm{V} \end{array}$$

If you were to look up the half reaction for zinc, you would notice its order is reversed and its electrode potential is -0.763.



It is impossible to measure only the electromotive force of a half reaction, therefore a reference standard was created by which to compare half reactions.

If you notice $2H^+ = 0.00$ in the electromotive series listed in Table 4-2. The universally accepted reference electrode is the standard hydrogen electrode (*SHE*)

$$H^+ + e^- \rightarrow \tfrac{1}{2}H_{2(g)}$$

At $P = 1atm$, $T = 25°C$ and $[H^+] = [H_2] = 1M \Rightarrow E° = 0.00$

Example 4-2

Calculate the E° for the oxidation of scandium (Sc).

Scandium gives up 3 electrons during oxidation.

$$Sc^{3+} + 1.5H_{2(g)} \leftrightarrow Sc + 3H^{+}$$

$$\Delta G_R = [(0.00) + (3)(0.00) – [(-586.6) + (1.5)(0.00)] = 586.6 kJ / mol$$

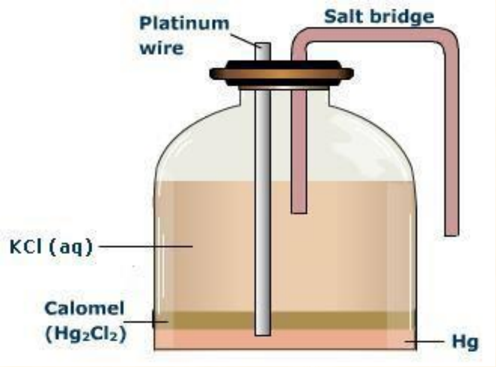
$$E^\circ = - \Delta G_R / n\mathcal{F} = -(586.6) / (3)(96.42) = - 0.03 V$$

Because the *SHE* is difficult to prepare and maintain, a calomel electrode is often used instead.

The **calomel electrode (SCE)** is a reference electrode based on the reaction between elemental mercury and mercury(I) chloride. The aqueous phase in contact with the mercury and the mercury(I) chloride (Hg_2Cl_2, "calomel") is a saturated solution of potassium chloride in water.

$$Hg_2Cl_2 + 2e^- \leftrightarrow 2Hg + 2Cl^-$$

*At standard conditions, the potential of the saturated calomel electrode should be +0.241 V versus the *SHE*.



Balancing Oxidation – Reduction Equations

1. Determine the valence numbers (charge) for all the elements involved in the reaction. (I like to set up a chart.)
2. Determine the number of electrons given off and taken up in the reaction. Balance the transfer of electrons.
3. Balance the elements, except oxygen and hydrogen, on both sides of the equation.
4. Balance the number of oxygen atoms by adding H_2O.
5. Balance the number of hydrogen atoms by adding H^+.

Example 4-3

Acid mine drainage is caused by the oxidation of pyrite when it comes in contact with water containing dissolved oxygen.

$$FeS_{2(pyrite)} + O_2 \rightarrow Fe(OH)_{3(ppt)} + SO_4^{2-}$$

Both Fe and S are oxidized.

Step 1: Determine the valence numbers for all of the elements involved in the reaction.

$$Fe^{2+} \rightarrow Fe^{3+} + e^-$$

$$S^- \rightarrow S^{6+} + 7e^-$$

$$FeS_{2(pyrite)} + O_2 \rightarrow Fe(OH)_{3(ppt)} + SO_4^{2-}$$

Step 2: Determine the number of electrons given off and taken up in the reaction. Balance and transfer electrons.

Recall from step 1 that Fe releases 1 electron and S releases 7 electrons. Therefore, the breakdown of one pyrite molecule releases 15 electrons. Now, where do they go?

Each oxygen receives 2 electrons, thus, 4 electrons are consumed by the O_2 molecule. This means we have accounted for $^4/_{15}$ of FeS_2's electrons.

$$^4/_{15}FeS_2 + O_2 \rightarrow Fe(OH)_{3(ppt)} + SO_4^{2-}.$$

To avoid fractions we set the equation to:

$$4FeS_2 + 15O_2 \rightarrow Fe(OH)_{3(ppt)} + SO_4^{2-}$$

On to Step 3…

Step 3: Balance the elements, except H & O on both sides of the equation.

$$4FeS_2 + 15O_2 \rightarrow 4Fe(OH)_{3(ppt)} + 8SO_4^{2-}$$

Step 4: Balance the number of oxygen atoms by adding H_2O.

$$4FeS_2 + 15O_2 + 14H_2O \rightarrow 4Fe(OH)_{3(ppt)} + 8SO_4^{2-}$$

Step 5: Balance the number of hydrogen atoms by adding H+.

$$4FeS_2 + 15O_2 + 14H_2O \rightarrow 4Fe(OH)_{3(ppt)} + 8SO_4^{2-} + 16H^+$$

You will notice from the reaction that a great deal of H^+ are released with the oxidation of pyrite. That is why we call it *acid* mine drainage!


ARGO
TUNNEL
ARGO

The Nernst Equation and Eh

Consider the following generic redox reaction:

$$aA_{ox} + bB_{red} \leftrightarrow cC_{red} + dD_{ox} \Rightarrow$$

$$\Delta G_R = \Delta G_{R_o} + RT \cdot \ln([C_{red}]_c[D_{ox}]_d / [A_{ox}]_a[B_{red}]_b) \Rightarrow$$

$E = E^\circ - (RT / n\mathcal{F})(\ln K)$ = The Nernst Equation which can be used to calculate the *emf* of an oxidation – reduction reaction under any conditions.

Using log instead of ln, the Nernst equation reads:

$$E = E^\circ - (0.0592 / n)(\log K) =$$

$$E^\circ + \frac{0.0592}{n} \cdot \log\left(\frac{\text{activity product of oxidized species}}{\text{activity product of reduced species}}\right)$$

Example 4-4

Calculate the emf for the half reaction

$$Mn^{3+} + e^{-} \rightarrow Mn^{2+}$$

Combining this reaction with the hydrogen electrode yields:

$$Mn^{3+} + \frac{1}{2} H_{2(g)} \leftrightarrow Mn^{2+} + H^{+}$$

For this reaction,

$$\Delta G_R = [(-228.1) + (0.00)] - [(-84.8) + (\frac{1}{2})(0.00)] = -143.3 \text{ kJ / mol}$$

$$E° = -(-143.3) / (1)(96.42) = 1.49V$$

$$E = 1.49 + (0.0592/1)(\log([Mn^{3+}][H_{2(g)}]^{\frac{1}{2}} / [Mn^{2+}][H^{+}])$$

Remember: $[H_{2(g)}] = [H^{+}] = 1$. $\therefore$ The $[Mn^{3+}]/[Mn^{2+}]$ must be determined by the electromotive force of the system.

For example, groundwater has E = 0.00V, and surface water has E = 0.80 V.

What would happen when groundwater is pumped to the surface?

At E = 0.00

$\log([Mn^{3+}] / [Mn^{2+}]) = (E - 1.49)/0.0592 = (0 - 1.49)/0.0592$

$= -25.2.$

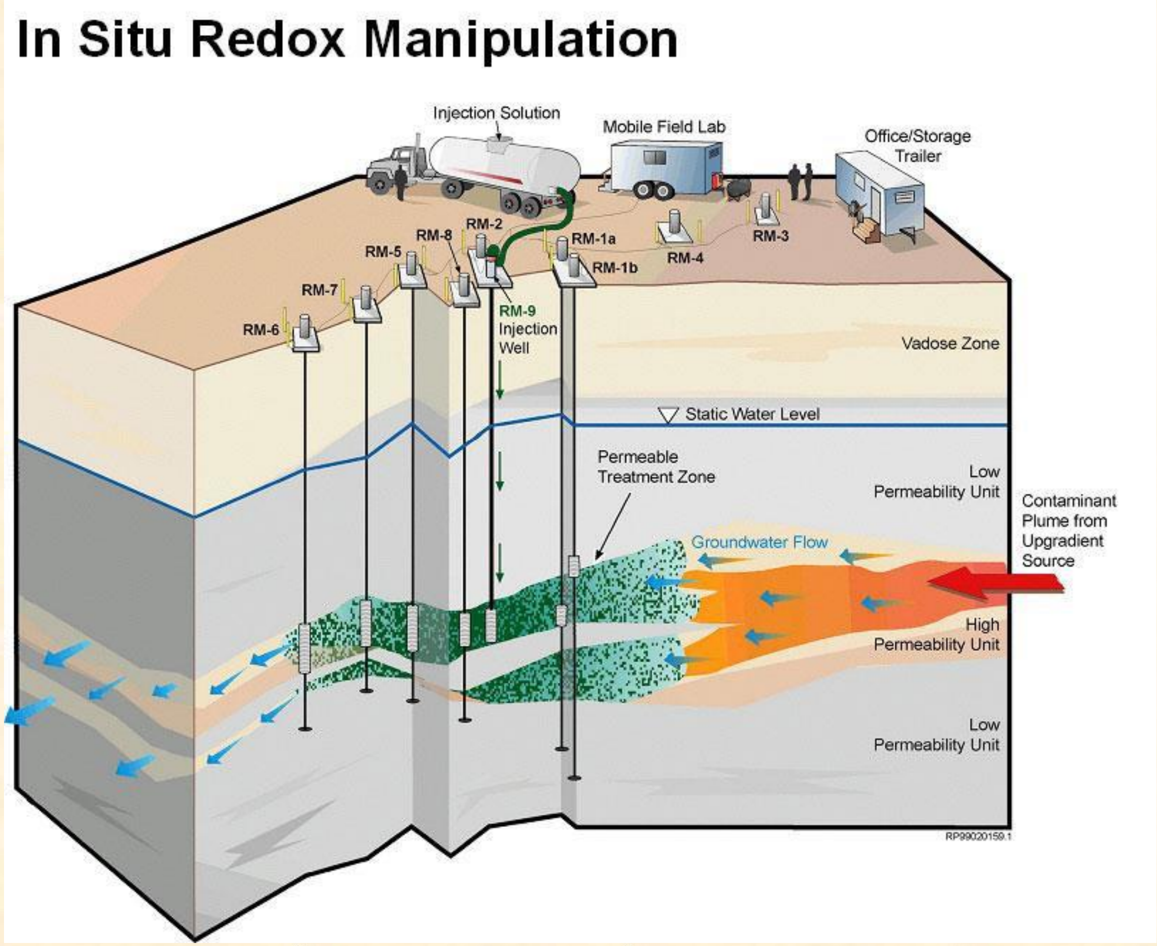
At E = 0.80V

$\log([Mn^{3+}] / [Mn^{2+}]) = (E - 1.49)/0.0592 = (0.80 - 1.49)/0.0592$

$= -11.7.$

When the groundwater is exposed to the oxidizing surface environment, Mn^{3+} increases relative to Mn^{2+}.

What we are looking at here is an activity ratio. So when E = 0.8, the amount of Mn^{3+} increases with respect to Mn^{2+}.



Eh is the electromotive force of any reaction measured relative to the standard hydrogen electrode. Eh is an environmental parameter that reflects the overall oxidation-reduction potential of a natural system relative to the hydrogen electrode.

Measurements of *emf* in the field are often made between a Pt electrode and a reference electrode. The measurements are then corrected by:

$$Eh = E_{meas} - E_{ref}$$

Example 4-5

Calculate the Eh for a water sample at 25°C for which $[Mn^{2+}] = 10^{-3}$ mol /L and $[Mn^{3+}] = 10^{-14}$ mol /L (Using the data from Example 4-4)

$Eh = 1.49 + 0.0592 \log[Mn^{3+}] - 0.0592 \log[Mn^{2+}]$

$= 1.49 + 0.0592 \log[10^{-14}] - 0.0592 \log[10^{-3}] = 0.84V$

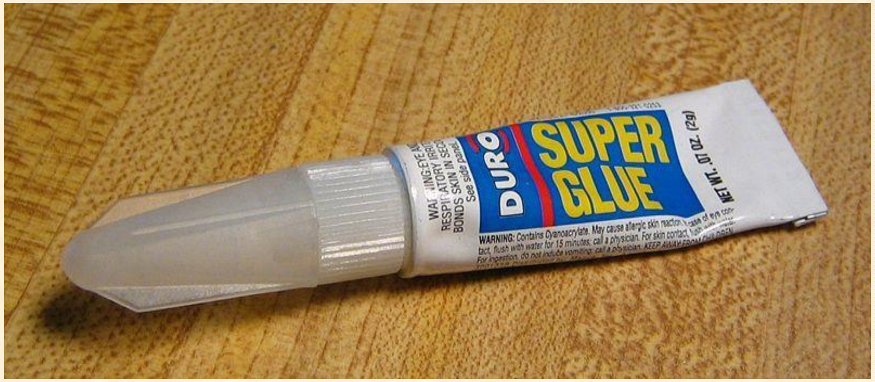
Now, a direct measurement is made using a calomel electrode as the reference electrode. The measured Eh is 901mV. The corrected Eh is

$Eh = Eh_{meas} - Eh_{ref}$ = 901mV – 244mV = 657mV or 0.657V

$0.84 \neq 0.657$

Why would the measured Eh not equal the calculated Eh?

Mn is an example of an **electroactive species**—electrons are easily exchanged at the surface of an Eh electrode. If the water sample was largely composed of electroactive species, then there should be good agreement between the measured and calculate Eh.



If, however, the water contains a significant amount of **nonelectroactive species**—electrons are not easily exchanged at the surface of an Eh electrode, then the sample would contain mixed potentials, because the nonelectroactive species are not in equilibrium with the Eh electrode.

Oxidation Reduction Reactions and pe

An alternate way of looking at oxidation-reduction is through the concept of electron activity (pe).

$$pe = -\log[e^-].$$

For example considering the following electrode:

$$Fe^{3+} + e^- \leftrightarrow Fe^{2+}$$

$$K = [Fe^{2+}] / [Fe^{3+}][e^-]$$

pe° = (1/n)(logK) where pe° is the pe in the standard state.

Under conditions other than the standard state:

$$pe = pe^\circ + (1/n)\log\left(\frac{\text{activity product of oxidized species}}{\text{activity product of reduced species}}\right)$$

Eh and pe are related as follows:

$$Eh = (2.303RT/\mathcal{F})(pe)$$

And at 25°C

$$Eh = 0.059pe$$

For example:

If, at 25°C, Eh = 1.10V, what is [e-]?

$$pe = 1.10 / 0.059 = 18.6$$

$pe = -\log[e^-]$, so $[e^-] = 10^{-18.6}$.

Eh and pH

Stability limits for natural waters at the earth’s surface in terms of Eh and pH at 25°C.

Think of the water electrode:

$$2H^+ + \frac{1}{2}O_2 + 2e^- \leftrightarrow H_2O$$

$$\Delta G_R = -237.14 \text{ kJ mol}^{-1} \quad E^o = 1.23 \text{ V}$$

Given the Nernst Equation:

$$Eh = 1.23 + (0.0592/2)\log([O_2]^{\frac{1}{2}}[H^+]^2)$$

After some fancy mathematical manipulation you would derive:

$$Eh = 1.23 + 0.0148\log[O_2] - 0.0592pH$$

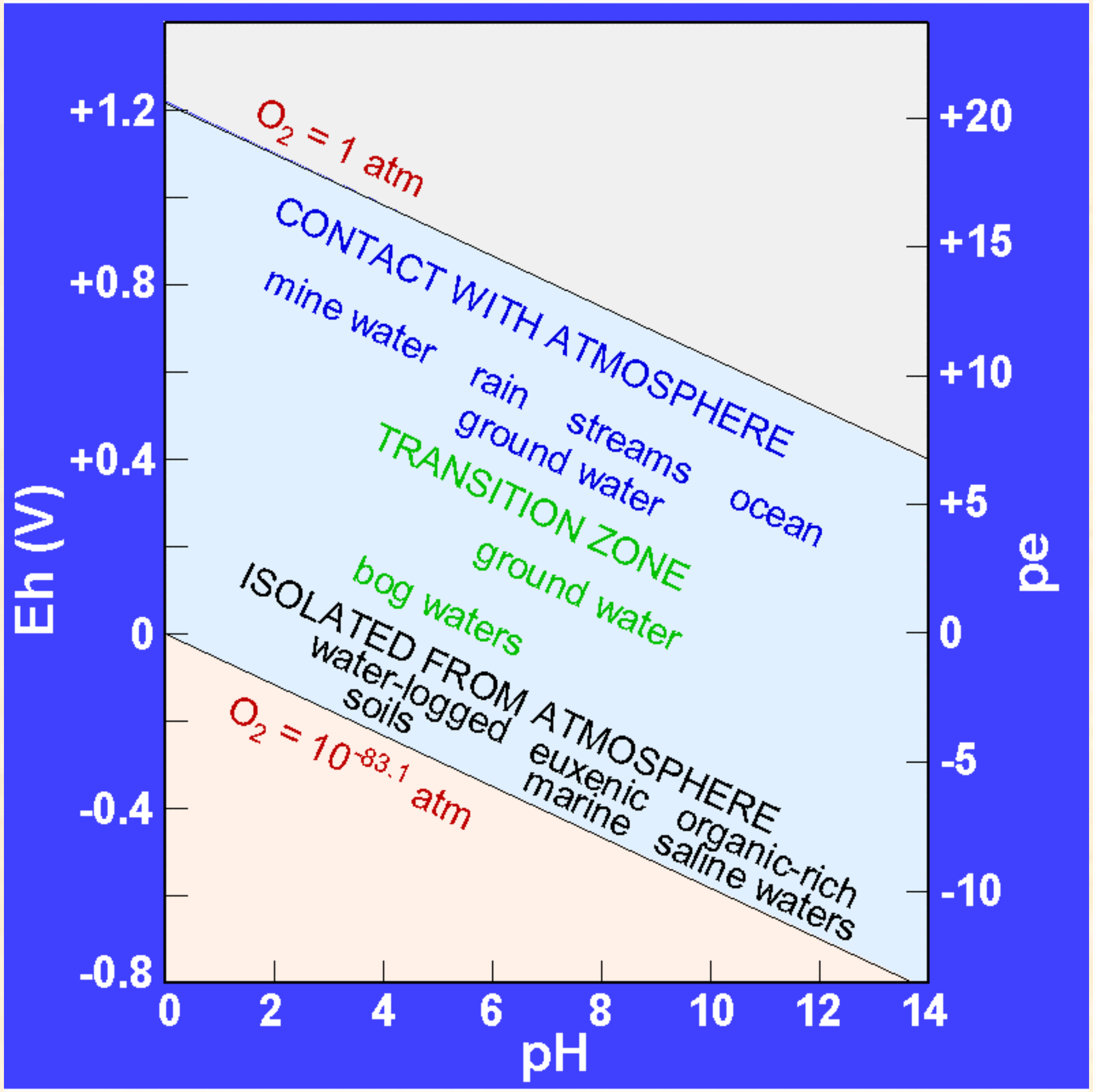
Now, let’s consider this equation: $2H_2O_{(l)} \rightleftharpoons O_{2(g)} + 2H_{2(g)}$

The Eh – pH diagram

The upper limit of H_2O is set where $P_{O_2} = 1$; and the lower limit is set where $P_{H_2} = 1$.

In the case of $P_{O_2} = 1$, $[H_2] = 10^{-41.65}$. When $P_{H_2} = 1$, $[O_2] = 10^{-83.1}$

Neither gas can have a partial pressure greater than 1.



$$Eh = 1.23 + 0.0148\log[O_2] - 0.0592pH$$

How are Eh and pH related?

Consider the following electrode:

$$Fe^{2+} + 2e^{-} \rightarrow Fe \quad \textit{emf} = -0.41V$$

And the standard:

$$H_2 \rightarrow 2H^{+} + 2e^{-} \quad \textit{emf} = 0.00V$$

Put them together in the equation:

$$2H^{+} + Fe \rightarrow H_2 + Fe^{2+}$$

$$Eh = E° + (0.0592/n)([Fe^{2+}] / [H^{+}]^{2}).$$

Recall pH = $-\log[H^{+}]$

Therefore we can find Eh if we also know $[H^{+}]$

The upper and lower limits of water well-define the boundaries of most other naturally occurring substances.

Given the other half reactions with Fe & H_2, we can develop other stability boundaries and place them within a diagram.

Let's continue to construct the Fe Eh-pH diagram with the reduction of magnetite (Fe_3O_4)

$$Fe_3O_4 + 8e^- + 8H^+ \rightleftharpoons 3Fe + 4H_2O$$

$Fe_3O_4 + 8e^- + 8H^+ \leftrightarrow 3Fe + 4H_2O$

$\Delta G_R = 64.2 \text{kJ mol}^{-1}$ $E^\circ = -0.083\text{V}$

Eh = -0.083 – 0.0592pH

http://geology.com/rocks/sedimentary-rocks.shtml

Next we look at hematite (Fe_2O_3)

$3Fe_2O_3 + 2e^- + 2H^+ \leftrightarrow 2Fe_3O_4 + H_2O$

$\Delta G_R = -34.2 \text{kJ mol}^{-1}$ $E^\circ = 0.18\text{V}$

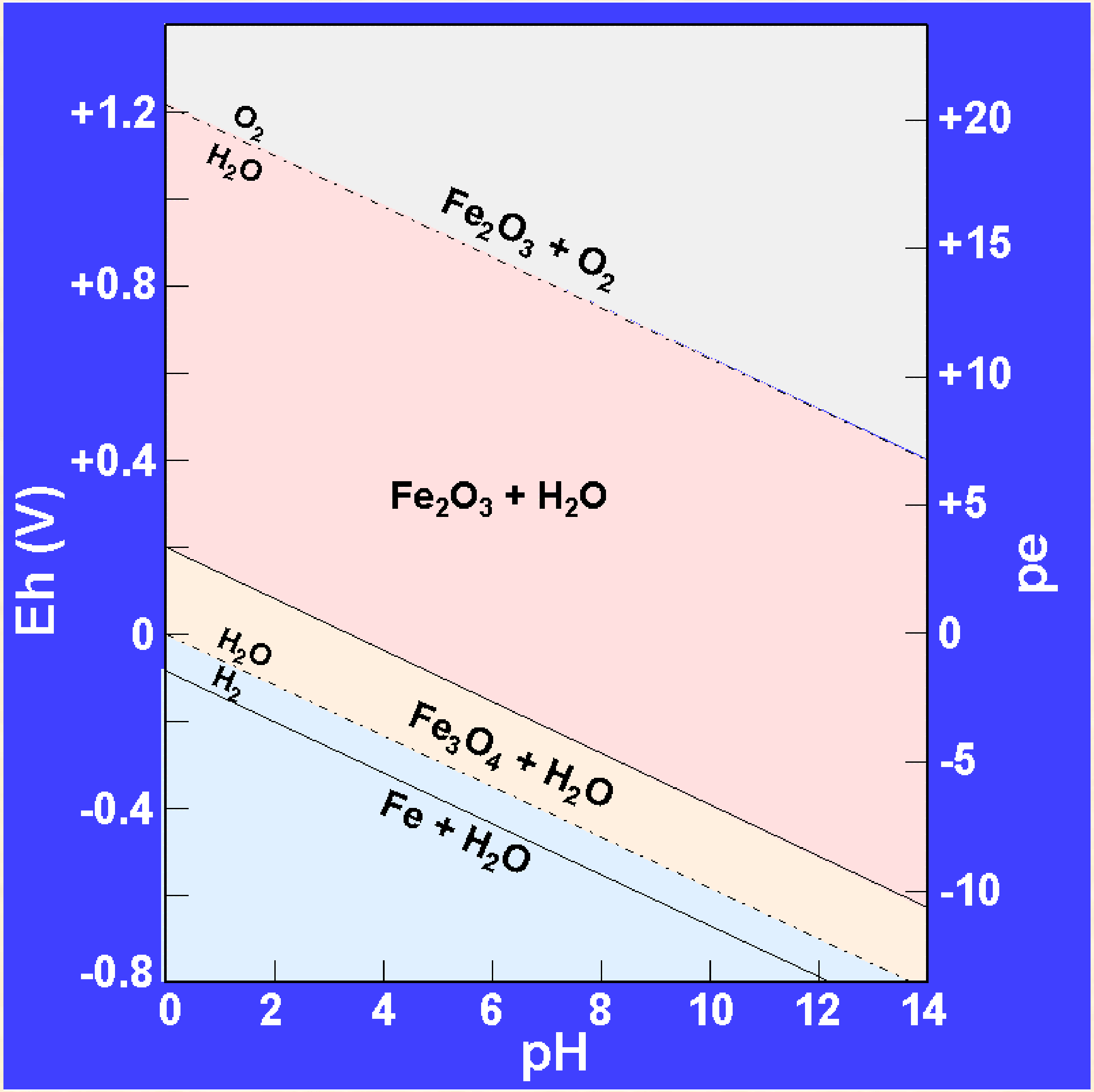
Eh = 0.18 – 0.0592pH

Iron Eh – pH diagram

Iron can exist in the natural environment in three oxidation states: 0, 2^+ & 3^+

Fe_3O_4 is the mineral *Magnetite* and Fe_2O_3 is the mineral *Hematite*.

Note that native iron does not coexist with water in the natural environment.



Let's consider the Eh – pH when dealing with specific ions in solution and vary the activity of the ions. For example:

$$\mathrm{Log}[\mathrm{Fe}^{3+}] + 3\mathrm{pH} = -1.95 \text{ and}$$

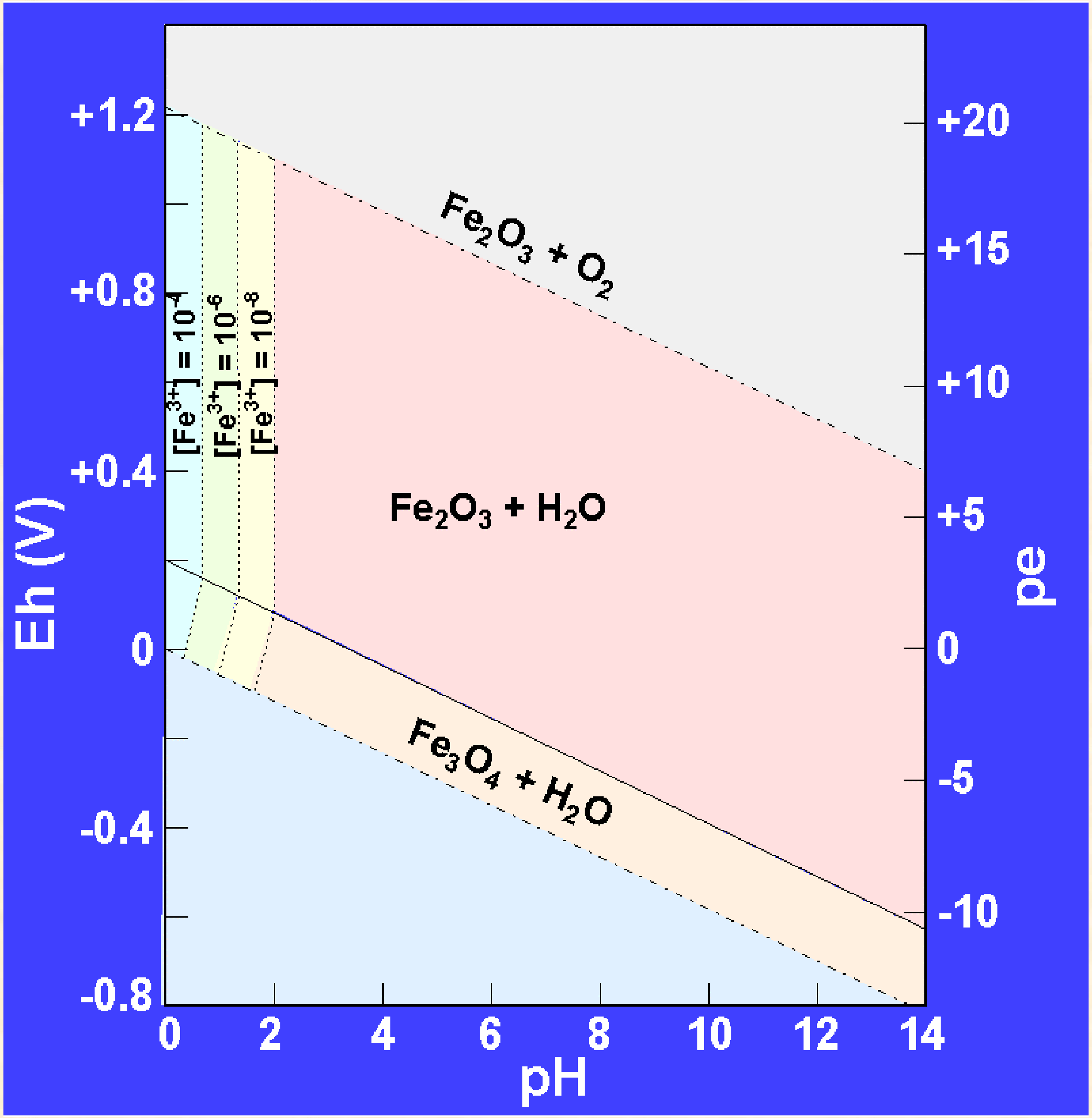
$$\mathrm{Eh} = 0.89 - 0.237\mathrm{pH} - 0.0888\log[\mathrm{Fe}^{2+}]$$

When dealing with the $[\mathrm{Fe}^{3+}]$ we end up with concentration dependent upon pH, but not Eh. That is because hematite has the Fe^{3+} charge and this does not change when the ions are dissociated.

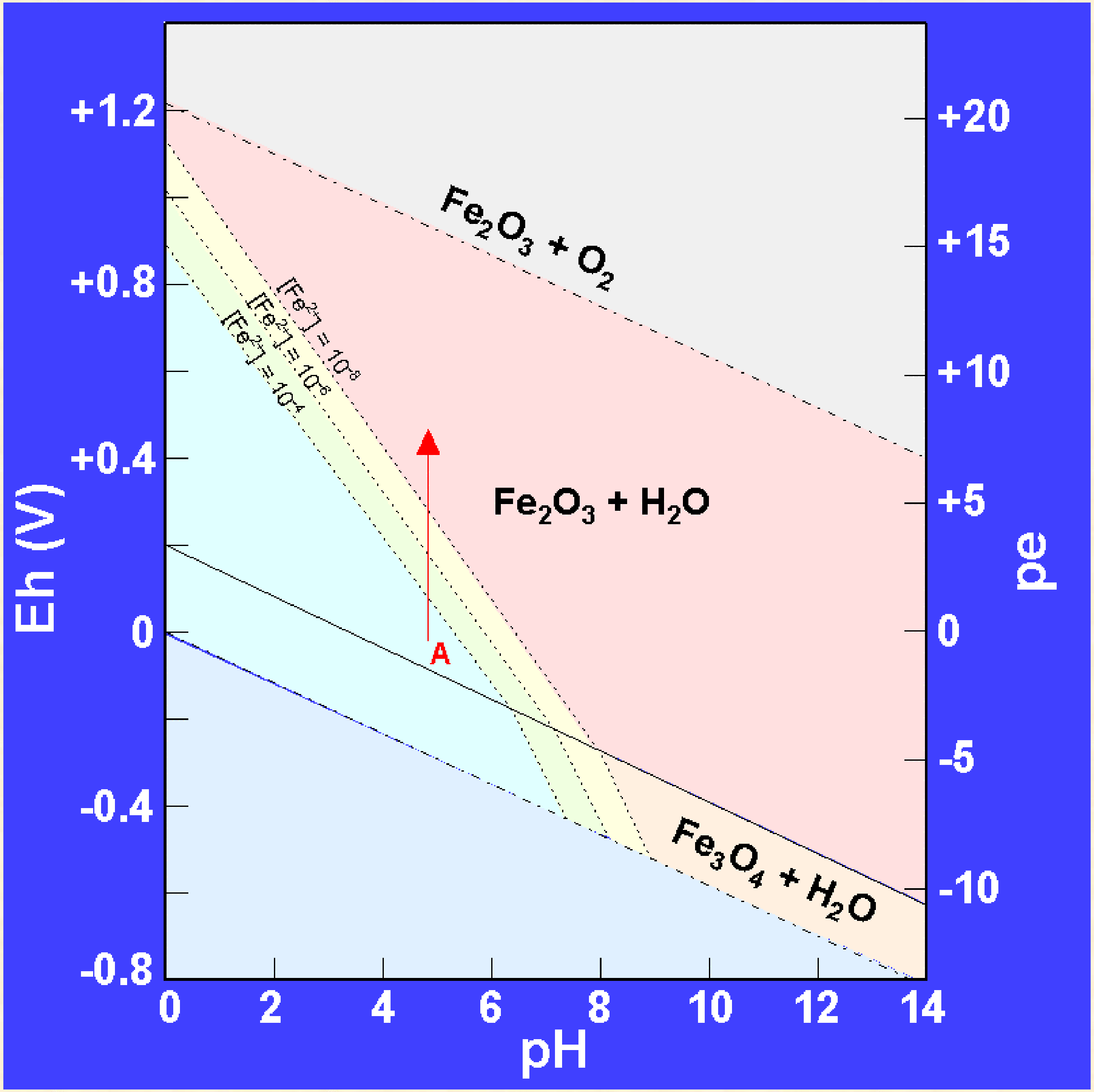
With $[\mathrm{Fe}^{2+}]$ the concentration is dependent upon both Eh and pH. (Magnetite contains both Fe^{3+} and Fe^{2+} ions.)

The resulting lines of varying concentrations are the contour lines on the diagram.

Eh-pH diagram showing variation in [Fe^{3+}], in mol L^{-1}, for a solution coexisting with hematite or magnetite. Only at very low pH values does Fe^{3+} have a significant activity.

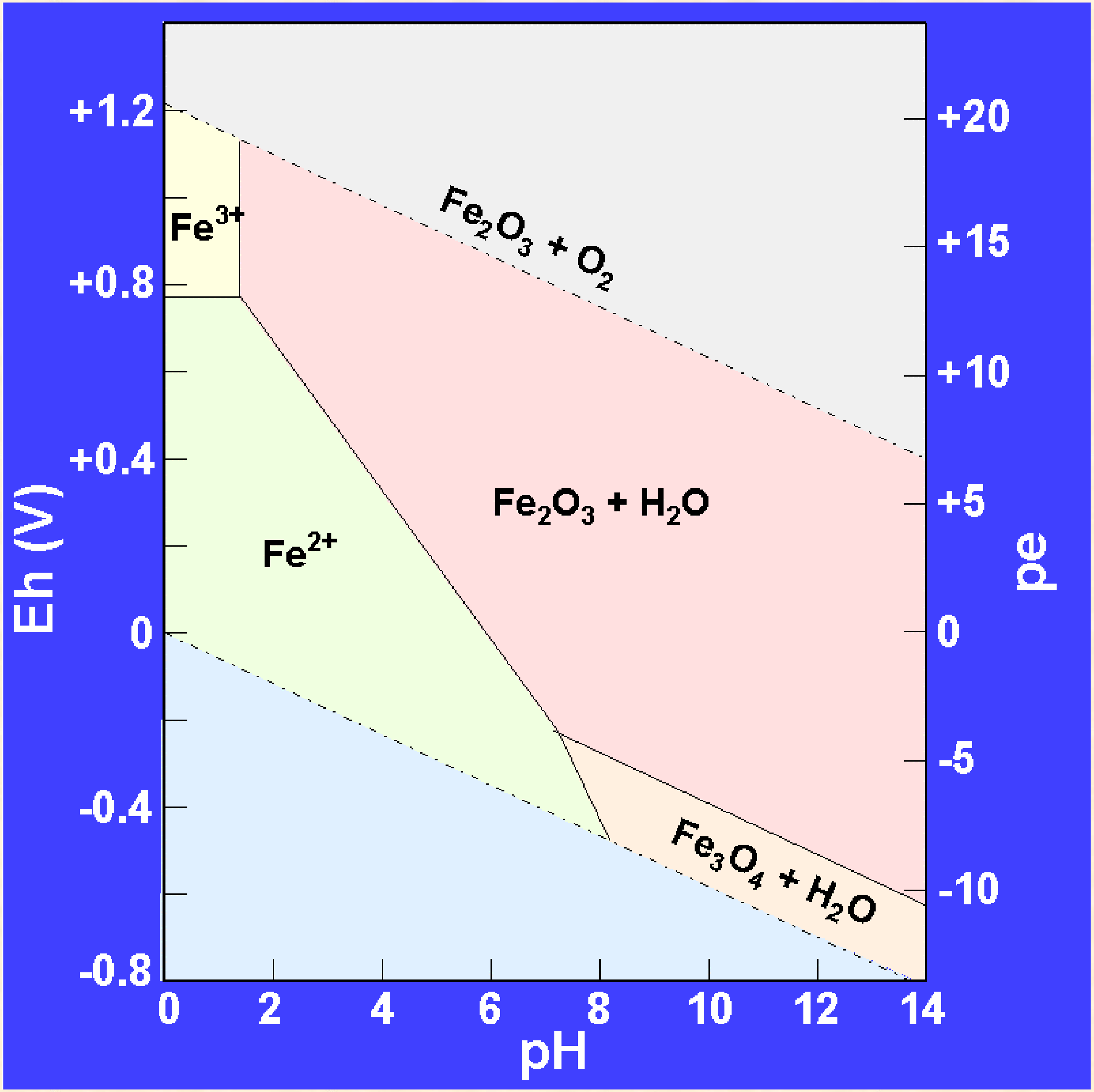


Eh-pH diagram showing the variation in [Fe^{2+}], in mol L^{-1}, for a solution coexisting with hematite or magnetite. The arrow indicates increasing oxidation.



Composite diagram showing the stability fields for hematite and magnetite as a function of Eh and pH.

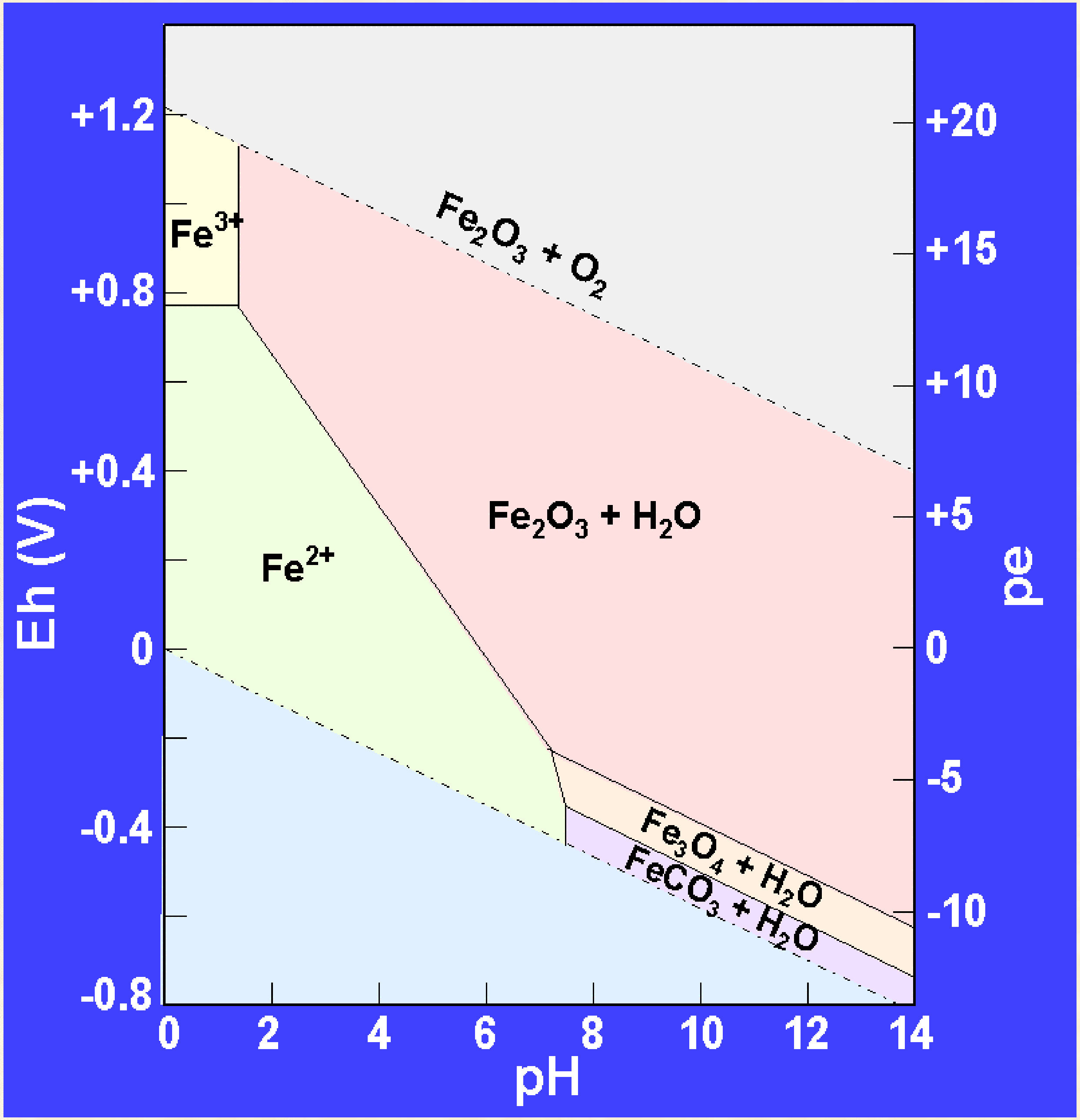
At Eh > 0.77V, Fe^{3+} is more abundant than Fe^{2+}.



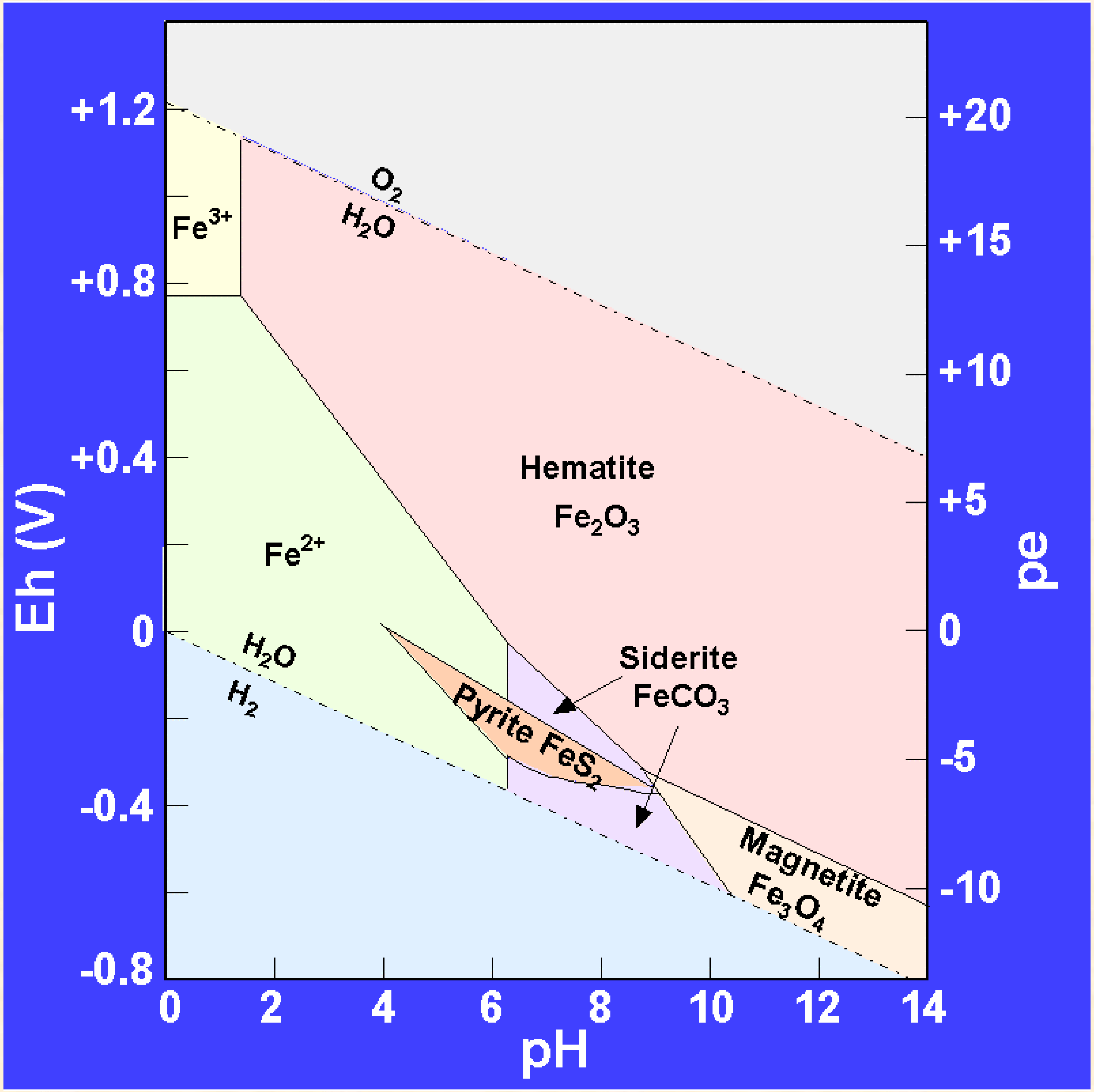
Composite Eh-pH diagram showing the stability fields of hematite, magnetite, and *siderite ($FeCO_3$)* as a function of Eh and pH.

For siderite, we must consider the atmospheric P_{CO_2}. This gives us the following formula:

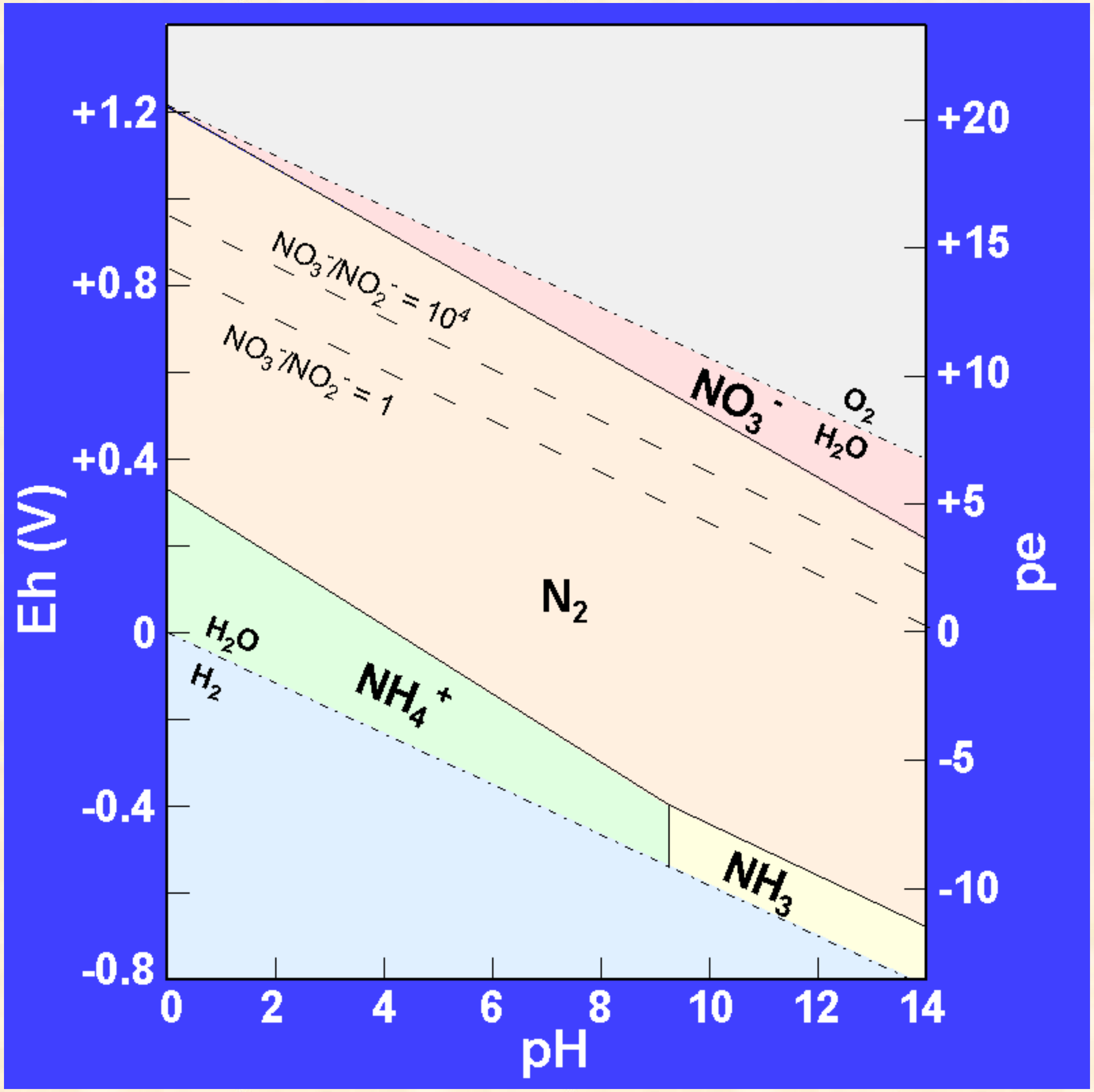
$$Eh = 0.0374 – 0.0592pH$$



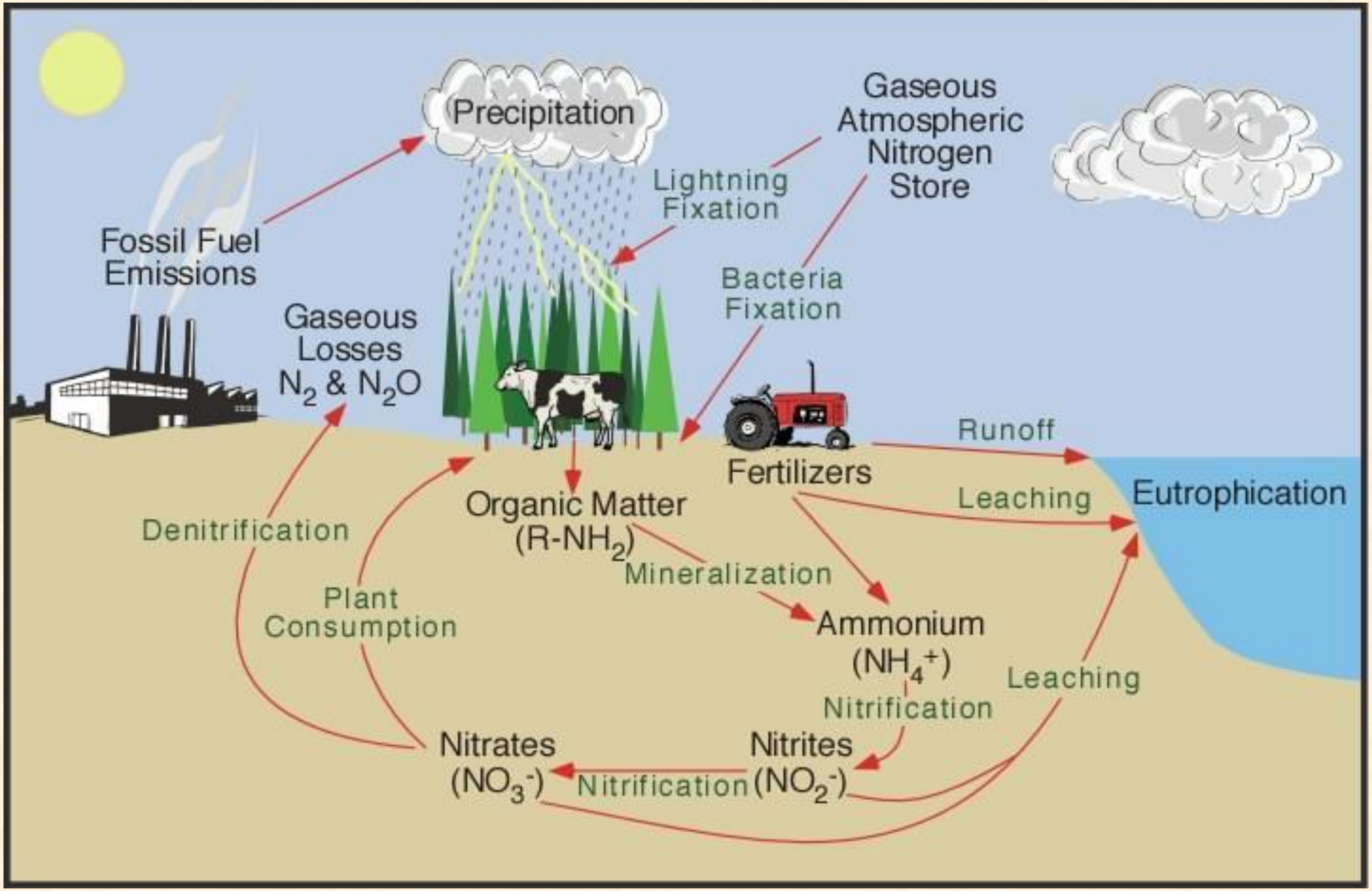
Composite Eh-pH diagram showing the stability relations for the iron oxides, carbonates, and sulfides in water at 25°C.



The same type of diagram can be applied to Nitrogen. In this case we only consider gaseous and aqueous species.



How do Eh – pH conditions apply to the natural nitrogen cycle?



The role of microorganisms in oxidation – reduction reactions

In the natural environment, microorganisms play an important role in facilitating oxidation – reduction reactions as catalysts. Think back to kinetics…

A **Catalyst** is a substance that speeds up a reaction ***without*** being consumed in the reaction.

For example: It has been reported that sulphide oxidation catalysed by *Thiomicrospira ferrooxidans* may have reaction rates six orders of magnitude (i.e. 1,000,000 times) greater than the same reactions in the absence of the bacteria.

Procaryotes: microorganisms with simple cellular structure with rigid cell walls and lack a nucleus.

Archaebacteria: (a subgroup of procaryotes) inhabit extreme environments, similar to those that may have existed early in earth history, and are considered to represent ancient life- forms.

Methanogens: bacteria that produce methane.

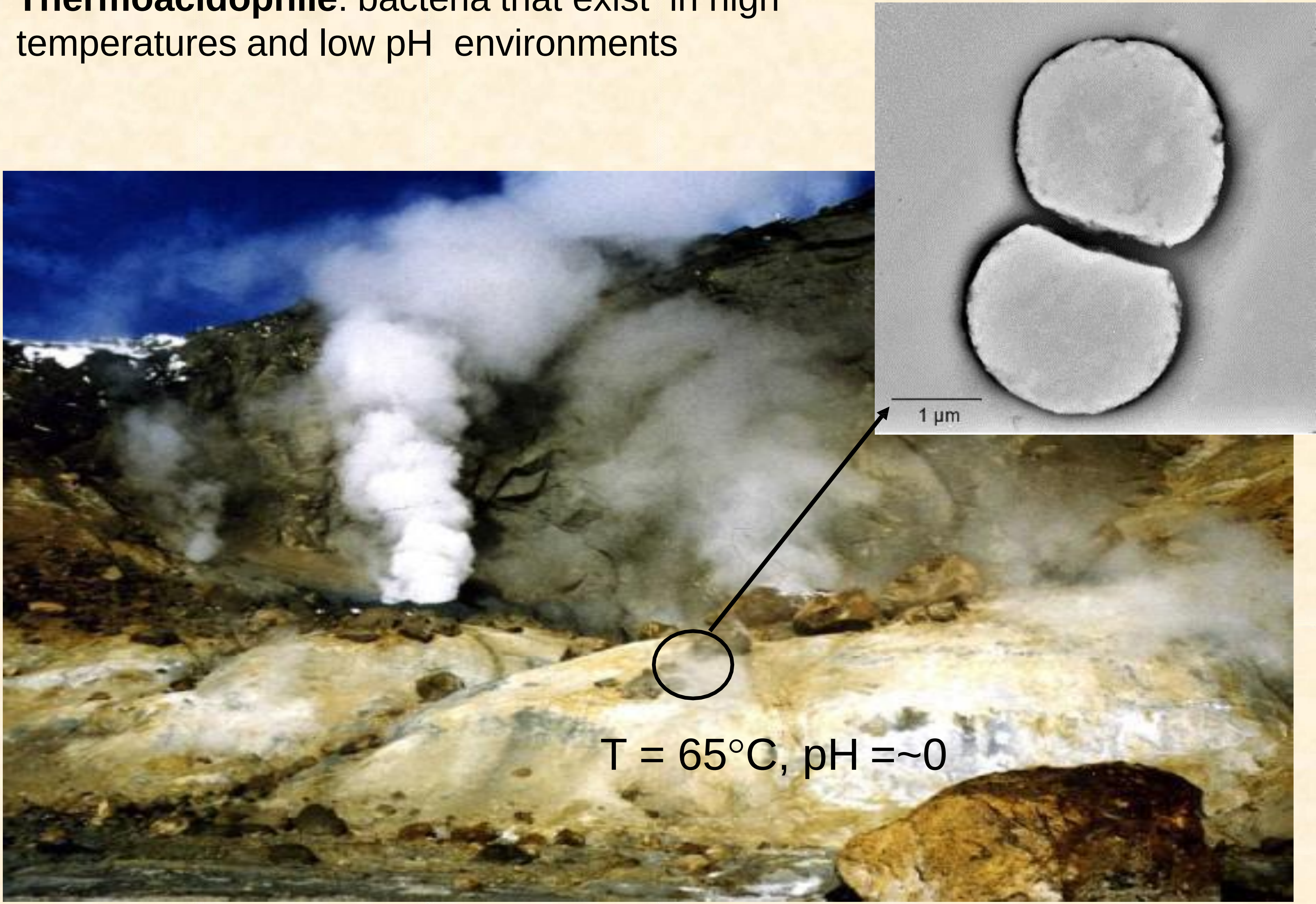
Halophiles: bacteria that exist in high salinity environments.

Thermophiles: bacteria that exist in high temperature environments.

Thermoacidophiles: bacterial that exist in high temperature and low pH environments.

Thermoacidophile: bacteria that exist in high temperatures and low pH environments

Picrophilus torridus



T = 65°C, pH =~0

Eucaryotes: have a true nucleus and a more complex structure than procaryotes. This more complex structure is represented by the presence of mitochondria, chloroplasts, and vacuoles and the compartmentalization of some key metabolic processes.

Autotrophs: obtain their carbon from CO_2, HCO_3^- or CO_3^{2-} and use external energy for the synthesis of organic compounds.

Photosynthesizers: use sunlight as the external energy source.

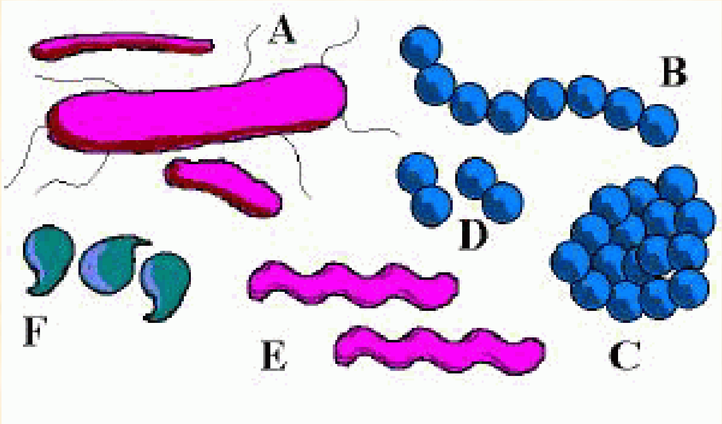
Chemosynthesizers: use chemical reactions involving various various inorganic molecules as the external energy source.

Photolithotrophs: photosynthetic autotrophs.

Chemolithotrophs: chemosynthetic autotrophs.

Heterotrophs: derive their energy from the oxidation of organic compounds and use previously synthesized carbon as their source of carbon.

Bacteria: single-celled organisms ranging in size from 0.2 to 50μm in diameter. They are the most abundant microorganisms in water and soil. The shape of bacterial cell is usually spherical, straight-rod, or curved rod. Because of their small size, they have a large surface-to-volume ratio and usually have a negative surface charge. With the exception of extreme environments inhabited by many of the archaebacteria, bacteria usually prefer neutral to slightly alkaline environments.



Actinomycetes: a class of unicellular organisms that show similarities to both fungi and bacteria. Their principle role is the degradation of existing organic compounds. Like bacteria, actinomycetes, prefer alkaline environments.

Fungi: multinucleate and do not have internal cell boundaries. The living mass of a fungus is bounded externally by a rigid wall composed of cellulose or chitin. The basic structure is tubular, often branched filament. Fungi use organic compounds as their carbon source and play a key role in the degradation of litter in the soil. Fungi prefer acidic environments.

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Algae: unicellular to complex multicellular varieties and vary in size from microscopic to large, plant-like structures. The main differences between the types of algae are biochemical:
(1) types of chlorophyll and other pigments, (2) chemical composition of the cell wall, and (3) chemical nature of stored foods. Algae convert inorganic carbon into organic compounds.

Protozoa: mostly unicellular organisms with animal-like characteristics and are commonly 5 to 50 μm in size. They are found either in water or in thin films of water on the surface of particles and are most abundant in warm, well-oxygenated environments of intermediate pH.

Photosynthesis

$$6CO_2 + 12H_2O + \text{photons} \rightarrow C_6H_{12}O_6 + 6O_2 + 6H_2O$$

Hydrogen sulfide chemosynthesis

$$6(CO_2) + 6(H_2O) + 3(H_2S) \rightarrow C_6H_{12}O_6 + 3(H_2SO_4)$$

This is how carbohydrates, subsequently used in respiration, are formed. –Think bottom of the food chain.

Microorganisms are either ***aerobes***—use molecular oxygen as their electron acceptor and can only function in the presence of O_2; ***faculative anaerobes***—can use either oxygen or other electron acceptors for oxidation; or ***obligate anaerobes***—can only function in the absence of oxygen.

Aerobes: microorganisms that directly use molecular oxygen as the electron acceptor for their oxidation reactions.

The model for aerobic respiration is the oxidation of the glucose molecule:

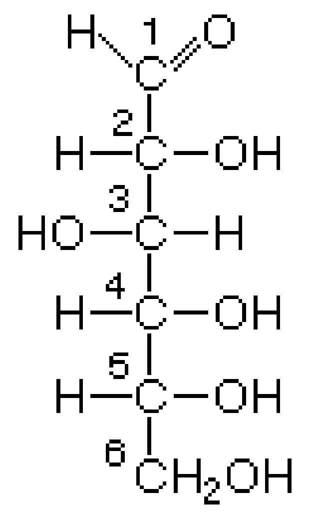
$$(1)\ C_6H_{12}O_6 + 6O_{2(g)} \rightarrow 6CO_2 + 6H_2O$$

This equation has an oxidation component,

$$(2)\ C_6H_{12}O_6 \rightarrow 6CO_2 + 12e^-$$

And a reduction component:

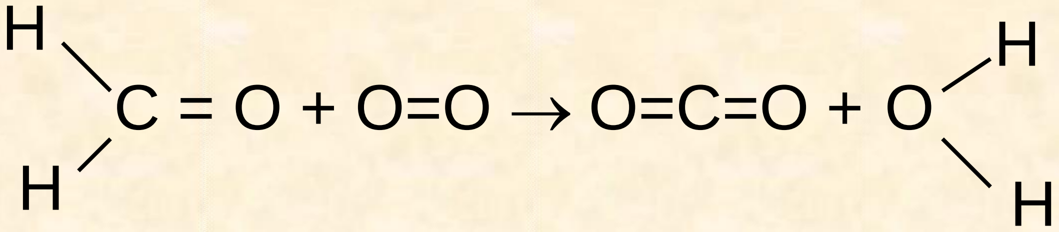
$$(3)\ 6O_2 + 12e^- \rightarrow 6H_2O$$



$CH_2O + O_2 \rightarrow CO_2 + H_2O + \text{energy}$

Let’s set up our chart and look at the simple structure carbohydrate reaction.

Element	Reactant	Product	Total # e^- lost / gained
C	+4	+4	0
O	0	-2	Gained 4
H	-1	+1	Lost 4



Now let’s look at aerobic respiration from an energy point of view.

Why breathe?

$$CH_2O + O_2 \rightarrow CO_2 + H_2O$$

$\Delta G_R = -501.8 \text{ kJ mol}^{-1}$

$\Delta H_R = -570.76 \text{ kJ mol}^{-1}$

This is an efficient, spontaneous, exothermic reaction.

Anaerobes: microorganisms that use other electron-poor species (H_2, SO_4^{2-}, NO_3^-) as the electron acceptor for their oxidation reactions.

Anaerobic respiration

Sulfate reduction: $\Delta G_R = -177.48$; $\Delta H_R = -1.86$

$$C_2H_3O_2^- + SO_4^{-2} + 3H^+ \rightarrow 2CO_2 + H_2S + 2H_2O$$

Nitrate reduction: $\Delta G_R = -160.6$; $\Delta H_R = -183.58$

$$NO_3^- + 2e^- + 2H^+ \rightarrow NO_2^- + H_2O$$

Methanogenesis: $\Delta G_R = -130.6$; $\Delta H_R = -252.91$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$

Recall that microorganisms act as catalysts for oxidation – reduction reactions. It is more accurate to say the microorganisms use catalysts, called enzymes, to facilitate the transfer of electrons.

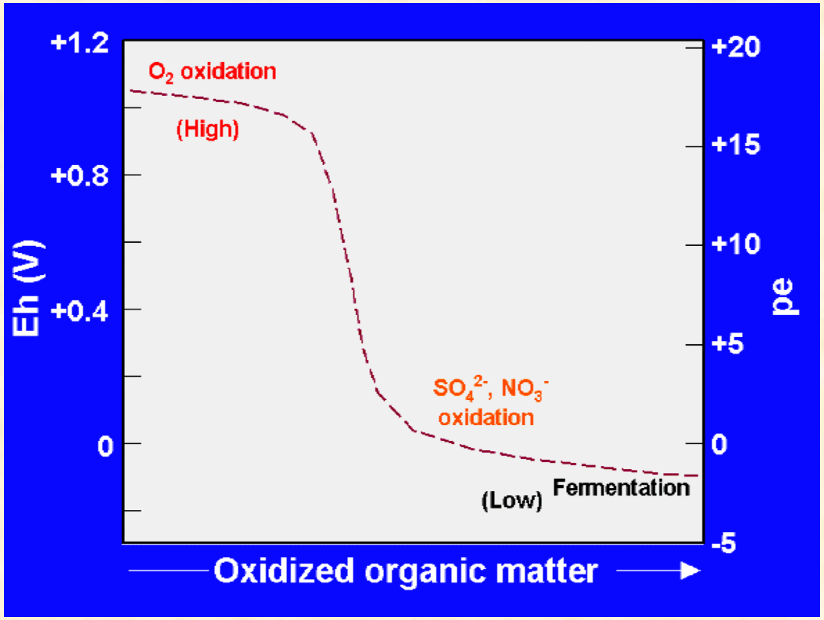
Enzymes are proteins that facilitate a fraction by forming a complex with the reaction that brings the reactants in to close proximity. Enzymes are usually specific to a particular substrate (i.e. oxygenases are enzymes that facilitate oxidation reactions and reductases are enzymes that facilitate reduction reactions.

Microorganisms can synthesize a new enzyme that can utilize a previously unavailable substrate…Think oil spill and microbial remediation of pollutants.

http://www.hullsenvironmental.com/emergency-response-oil-spill-clean-up

OIL EATERS: Newly discovered microbes (circled here in red) feast on specific hydrocarbons in the Gulf of Mexico oil spill. Image: © Science / AAAS

Redox buffering: when oxygen is present , in an aquatic environment the Eh is controlled by the oxygen—water half reaction. During the oxidation of organic matter, so long as measurable oxygen is present, there is very little change in Eh. When dissolved oxygen is no longer present, there is a rapid drop in Eh until the sulfate and nitrate oxidation— reduction reactions become important. When sulfates and nitrates have become exhausted, there is a further decline in Eh, until anaerobic biodegradation becomes important.



How would eutrophication relate to this process? Would a die-off be rapid or gradual?

Redox Interface: (redox front) a zone of rapidly changing Eh. This zone may be sharp and extend over a distance of only several millimeters, or it may extend over a distance of many meters or tens of meters. Redox interfaces occur where environments of very different oxidation–reduction potentials come into contact.