Advanced Water Quality

Class 23:

Redox Chemistry I

Topics

- Definitions and Terminology
- Oxidation state
- Half reactions and balancing redox reactions
- Determining energetic favorability of redox reactions
- Influence of solution conditions and chemical speciation on redox energetics

Redox processes

- Short for oxidation – reduction
- e^- transfer between reactants

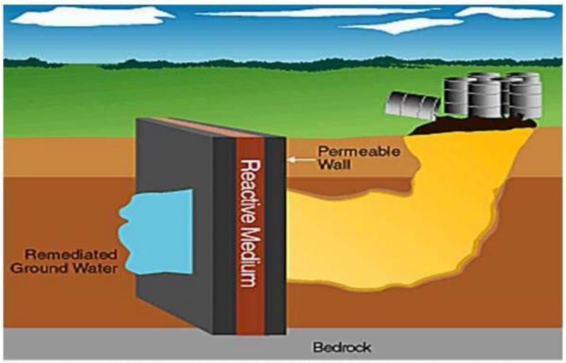
Disinfection

Biological WW treatment

Combustion & emissions

Air quality

Drinking water & sanitation in the developing world



Permeable reactive barriers have the potential to lower the cost and increase the effectiveness of groundwater cleanup.

Groundwater (bio)remediation

Bioenergy development

What does redox look like?

- Overall reaction consists to two coupled half reactions
  - One half reaction donates electrons (oxidation), the other accepts the electrons (reduction)

$$Y(0) \rightarrow e^- + Y(+I) \qquad \text{(Oxidation)}$$

$$X(0) + e^- \rightarrow X(-I) \qquad \text{(Reduction)}$$

$$\text{Overall:} \quad \underline{X(0) + Y(0) \rightarrow X(-I) + Y(+I)}$$

Oxidation states (not usually written explicitly)

Kinetic Limits on Redox Rxns

- Redox reactions often kinetically limited
- Non-equilibrium system (Q/K»1 or «1) often quite stable for long period of time
- Understanding redox equilibria still useful because it tells us the direction of spontaneous change
- Metabolic activities involve capturing the energy released in redox rxns
- Organisms have developed special catalysts, called enzymes, that reduce the kinetic inhibitions on redox rxns.

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- Definitions and Terminology
- **Oxidation state**
- Half reactions and balancing redox reactions
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- Influence of solution conditions and chemical speciation on redox energetics

Redox Chemistry: Oxidation State

- 2 or more atoms change oxidation state during a redox rxn

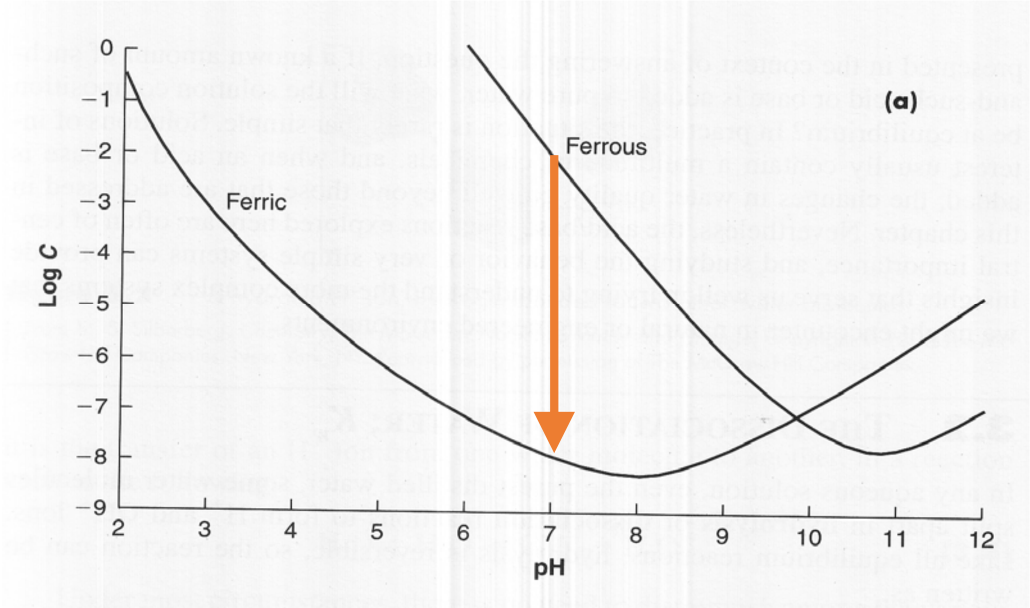
$$\left(\begin{array}{c}\text{formal}\\\text{oxidation}\\\text{state}\end{array}\right)=\left(\begin{array}{c}\#\text{ protons in}\\\text{atom's nucleus}\end{array}\right)-\left(\begin{array}{c}\#\text{ electrons}\\\text{assigned to}\\\text{the atom}\end{array}\right)$$

- **Reduction** = substance gains e^-
- **Oxidation** = substance loses e^-
- #e^- gained by reduced substance = #e^- lost by oxidized substances
- Many atoms of interest (C,N,O,S,Fe,Mn,Cl) exist in the environment in multiple stable oxidation states
- E.g., carbon in CO_2 has a higher oxidation state (+4) than in sugar (0). So sugar is oxidized to form CO_2

Element	Stable Oxidation States Under Environmental Conditions
C	**-4 to +4**
N	**-3 to +5**
O	**-2 to 0**
S	**-2,-1,0,+4,+6**
Cl	**-1**,0,+1,+3,+5,+7
Fe	**+2,+3,**+4,+5,+6
Mn	**+2,+3,+4**,+7
Co	**+2,+3**
Cr	**+3,+6**
As	**+3,+5**
P	-3,+3,**+5**
Hg	**0,+1,+2**
Bold = naturally-occurring members in abundance	

- Changes in oxidation state can have major impact on elemental properties

E.g., Aqueous solubility of Fe(III) & Fe(II) differ by orders of magnitude under most pH conditions



- During Fe removal we convert the Fe(II) present in groundwater to Fe(III) which is much less soluble
  - E.g., 6 order of magnitude drop in dissolved Fe at pH 7

- Changes in oxidation state can have major impact on elemental properties

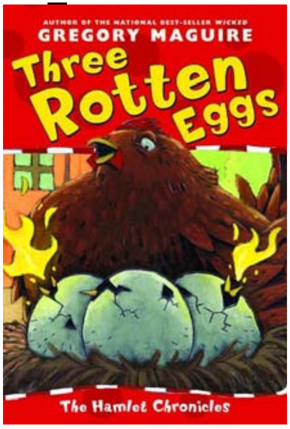
e.g. Volatility & Toxicity of Sulfur Species

S^{IV}: (sulfate, SO_4^{2-})

- highly water soluble
- non-volatile
- relatively non-toxic

S^{-II}: (hydrogen sulfide, H_2S; mercaptans $H_3C\text{-}SH$)

- Forms insoluble metal precipitates
- Strong abiotic reductant in natural systems
- Volatile
- Toxic



Clarifications

- Roman numerals represent the oxidation state of an element,
  - e.g., Fe(II) or Fe^{II}; Cd(II), Fe(III), S(-II)
  - Fe(II) ≠ Fe^{2+}
- There may be several species for a given oxidation state
  - E.g., Fe(II) includes Fe^{2+}, $FeOH^{+}$, $Fe(OH)_3^{-}$, $Fe(EDTA)^{2-}$, $FeH(EDTA)^{-}$, ….
- The statement, "there is 0.5 mM Fe(II) present" means $C_{T,Fe(II)} = 0.5$ mM = $[Fe^{2+}]+[FeOH^{+}]+[Fe(OH)_2^{0}]+…$
- The statement, "there is 0.5 mM total iron present" means $C_{T,Fe}$ = 0.5 mM = $C_{T,Fe(II)} + C_{T,Fe(III)} = [Fe^{2+}]+[FeOH^{+}]+…$

$$[Fe(OH)_2^{0}]+[Fe^{3+}]+[FeOH^{2+}]+[Fe(OH)_2^{+}]+…$$

Calculating Formal Oxidation States

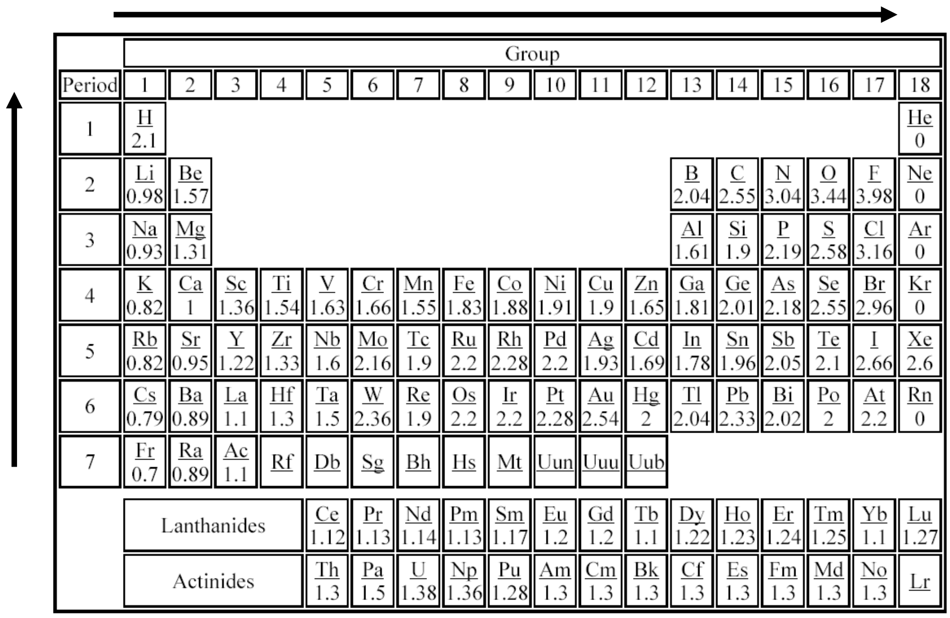
$$\begin{pmatrix}\text{formal}\\ \text{oxidation}\\ \text{state}\end{pmatrix} = \begin{pmatrix}\text{\# protons in}\\ \text{atom's nucleus}\end{pmatrix} - \begin{pmatrix}\text{\# electrons}\\ \text{assigned to}\\ \text{the atom}\end{pmatrix}$$

- Electronegativity approach
  - More electronegative elements will pull electron density of a bond towards themselves
  - For each bond formed with a less electronegative element, the atom will gain -1
  - Fore each bond formed with a more electronegative element, the atom will gain +1

Electronegativity

(Wikipedia) measure of the ability of an atom or molecule to attract electrons in the context of a chemical bond

- Add to formal charge -1 for each bond to less electronegative element, and +1 for each bond to more electronegative element
- Also add any charge on that group; Oxidation state = sum up the charges



	Group																	
Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H 2.1																	He 0
2	Li 0.98	Be 1.57											B 2.04	C 2.55	N 3.04	O 3.44	F 3.98	Ne 0
3	Na 0.93	Mg 1.31											Al 1.61	Si 1.9	P 2.19	S 2.58	Cl 3.16	Ar 0
4	K 0.82	Ca 1	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 1.9	Zn 1.65	Ga 1.81	Ge 2.01	As 2.18	Se 2.55	Br 2.96	Kr 0
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 2.2	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	La 1.1	Hf 1.3	Ta 1.5	W 2.36	Re 1.9	Os 2.2	Ir 2.2	Pt 2.28	Au 2.54	Hg 2	Tl 2.04	Pb 2.33	Bi 2.02	Po 2	At 2.2	Rn 0
7	Fr 0.7	Ra 0.89	Ac 1.1	Rf	Db	Sg	Bh	Hs	Mt	Uun	Uuu	Uub						
	Lanthanides				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				Th 1.3	Pa 1.5	U 1.38	Np 1.36	Pu 1.28	Am 1.3	Cm 1.3	Bk 1.3	Cf 1.3	Es 1.3	Fm 1.3	Md 1.3	No 1.3	Lr

Electronegativity increases
-From left to right due to increasing proton (nuclear) and electron (valence shell) charge
-From bottom to top due to proximity of valence e^- to protons in nucleus and less shielding from filled orbitals in between valence e^- and nucleus

Algorithm for Avg Oxidation States

Rule: Charge must be conserved

Conventions

1. Atoms in a pure element or mC such as H_2 have oxidation state of 0.
2. Oxidation state of monoatomic ions = ion charge.
3. **H** has an oxidation state of +1
4. **O** has an oxidation state of -2
5. **N** has an oxidation state of -3 when bonded to H or C
6. **S** has an oxidation state of -2 when bonded to H or C
7. **F** has an oxidation state of -1
8. **Cl, Br, I** have oxidation states of -1 except in compounds containing F or O (both of which possess higher electronegativities)

Application: Conventions are applied in order shown, but can be ignored if necessary to avoid violating the Charge conservation rule

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- **Half reactions and balancing redox reactions**
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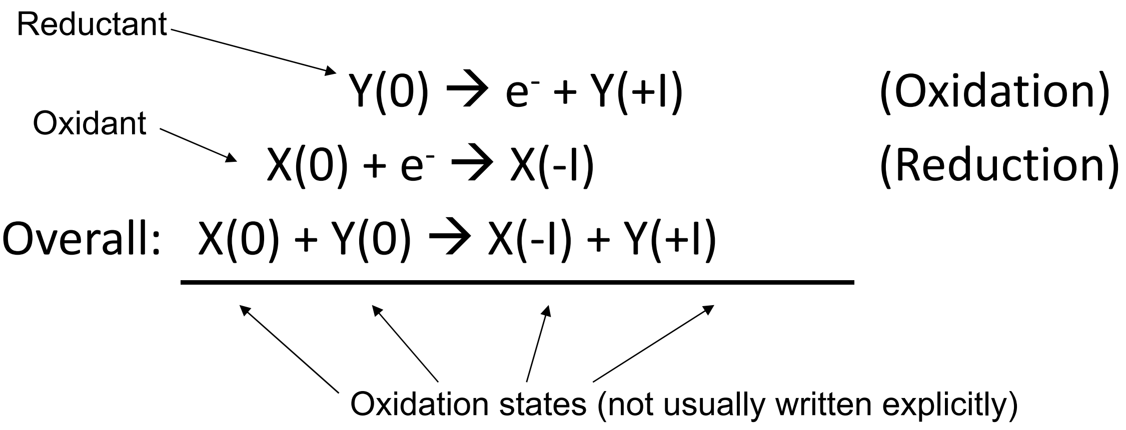
- Influence of solution conditions and chemical speciation on redox energetics

Half Reactions

- Overall reaction consists to **two coupled half reactions**
  - One half reaction donates electrons (oxidation), the other accepts the electrons (reduction)



Reductant

$Y(0) \rightarrow e^- + Y(+I)$ (Oxidation)

Oxidant

$X(0) + e^- \rightarrow X(-I)$ (Reduction)

Overall: $X(0) + Y(0) \rightarrow X(-I) + Y(+I)$

Oxidation states (not usually written explicitly)

- E.g., oxidation of Fe^{2+} by O_2:

OHR: $(Fe^{2+} = Fe^{3+} + 1e^-) \times 4$

RHR: $O_2 + 4H^+ + 4e^- = 2H_2O$

Overall: $4Fe^{2+} + O_2 + 4H^+ = 4Fe^{3+} + 2H_2O$

Fe (O.S. ↑ +2 → +3)

O (O.S. ↓ 0 ← -2)

- Balance overall rxn has no e^- on either side
- Tables of common half rxns available with thermodynamic parameters (redox potential)
- Can combine half reactions and evaluate whether overall rxn is energetically favorable ($\Delta E_{rxn} > 0$)

Anatomy of the half reaction

$$X_{ox} + \underset{\xleftarrow[\text{oxidation}]{}}{\overset{\xrightarrow{\text{reduction}}}{ne^- \;=}} X_{red}$$

Anatomy of the half reaction

$$\underbrace{X_{ox}}_{} + \overset{\xrightarrow{\text{reduction}}}{ne^- \;=}\; X_{red}$$

Substance gets reduced
Oxidant
Oxidizing agent
Electron acceptor
Higher oxidation state

Anatomy of the half reaction

$$X_{ox} + \underset{\xleftarrow[\text{oxidation}]{}}{ne^- \;=}\; \underbrace{X_{red}}_{}$$

Substance gets oxidized
Reductant
Reducing agent
Electron donor
Lower oxidation state

Balancing Redox Reactions

Consider oxidation of H_2S by HOCl

1. Identify what is oxidized and what is reduced:

H_2S oxidized & HOCl reduced

2. Write unbalanced form of half rxns

$H_2S = SO_4^{2-}$ (O.S. -2 to +6)

$HOCl = Cl^-$ (O.S. +1 to -1)

3. Balance atoms in the individual half rxns other than H and O:

$H_2S = SO_4^{2-}$

$HOCl = Cl^-$

4. Balance oxygens using H_2O:

$H_2S + \mathbf{4H_2O} = SO_4^{2-}$

$HOCl = Cl^- + \mathbf{H_2O}$

5. Balance hydrogens using H^+:

$H_2S + 4H_2O = \mathbf{10H^+} + SO_4^{2-}$

$HOCl + \mathbf{H^+} = Cl^- + H_2O$

Balancing Redox Reactions

6 (method 1). Balance charge using e^-:

$H_2S + 4H_2O = 10H^+ + SO_4^{2-} + \mathbf{8e^-}$

$HOCl + H^+ + \mathbf{2e^-} = Cl^- + H_2O$

6 (method 2). #e^- could have been determined earlier from changes in formal oxidation state of each half reaction:

$H_2S = SO_4^{2-}$ (O.S. -2 to +6) H_2S gives up $8e^-$

$HOCl = Cl^-$ (O.S. +1 to -1) HOCl gains $2e^-$

7. Multiply each half reaction by an appropriate integer so that each contains equivalent e^-:

1 x $(H_2S + 4H_2O = 10H^+ + SO_4^{2-} + 8e^-)$

4 x $(HOCl + H^+ + 2e^- = Cl^- + H_2O)$

8. Add the balanced half reactions:

$H_2S + 4HOCl + 4H^+ + 4H_2O = 4Cl^- + SO_4^{2-} + 10H^+ + 4H_2O$

$$\boxed{H_2S + 4HOCl = 4Cl^- + SO_4^{2-} + 6H^+}$$

Exercise: Write balanced reactions for the following processes:

1. Oxidation arsenite (H_3AsO_3) to arsenate ($HAsO_4^{2-}$) coupled to the reduction of the green oxidant ferrate (FeO_4^{2-}) to $Fe(OH)_3(s)$.

2. Anaerobic bioremediation of petroleum hydrocarbons: oxidative mineralization of benzene (C_6H_6) coupled with nitrate (NO_3^-) reduction to ammonium (NH_4^+).

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3. Denitrification in WWT: reduction of nitrate (NO_3^-) to nitrogen gas (N_2), coupled with mineralization of an electron donor, typically methanol (H_3COH).

4. Abiotic groundwater remediation: reduction of trichloroethene (C_2HCl_3) to acetylene (C_2H_2) coupled with the corrosion of zero-valent iron filings (ZVI; Fe^0) to $Fe(OH)_3(s)$.

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Evaluating Favorability of Redox Rxn

1st Approach: Same as Earlier

1. Obtain balanced overall redox rxn
2. Calculate ΔG^0_{rxn} using G_f^0 values

$$\Delta G^0_{rxn} = (\Sigma \nu_i G_{fi}^0)_{products} - (\Sigma \nu_i G_{fi}^0)_{reactants}$$

$$\Delta G^0_{rxn} = -RT\ln K_{eq}$$

3. Calculate **Q** for current conditions in solution and use this to calculate ΔG

$$\Delta G = \Delta G^0_{rxn} + RT\ln Q = RT\ln(Q/K_{eq})$$

ΔG:	< 0	0	> 0
Spontaneous Direction	→	@Equilibrium	←

- We can determine ΔG^0 values for half rxns because G_f^0 for $e^- = 0$ by convention
- If we know the value of ΔG^0 for two half rxns can quickly determine ΔG^0 for overall rxn
- Consider Fe^{2+} oxidation by $MnO_2(s)$:

OHR: $Fe^{2+} + 3H_2O = Fe(OH)_3(s) + 3H^+ + e^-$

$$\Delta G^0_{OHR} = \underset{Fe(OH)_3(s)}{-699\ \text{kJ/mol}} + \underset{H^+}{3(0)} + \underset{e^-}{(0)} - \underset{Fe^{2+}}{(-78.87)} - \underset{3H_2O}{3(-237.18)}$$

$$= +91.41\ \text{kJ/mol}$$

RHR: $MnO_2(s) + 4H^+ + 2e^- = Mn^{2+} + 2H_2O$

$$\Delta G^0_{RHR} = \underset{Mn^{2+}}{-228.0} + \underset{H_2O}{2(-237.18)} - \underset{MnO_2(s)}{(-465.1)} - \underset{H^+}{4(0)} - \underset{e^-}{2(0)}$$

$$= -237.26\ \text{kJ/mol}$$

	ΔG^0
OHR: $Fe^{2+} + 3H_2O = Fe(OH)_3(s) + 3H^+ + e^-$	+91.41 kJ/mol
RHR: $MnO_2(s) + 4H^+ + 2e^- = Mn^{2+} + 2H_2O$	-237.26 kJ/mol

To balance, multiply OHR x 2

	ΔG^0
$2(Fe^{2+} + 3H_2O = Fe(OH)_3(s) + 3H^+ + e^-)$	2(+91.41) kcal/mol
$(MnO_2(s) + 4H^+ + 2e^- = Mn^{2+} + 2H_2O)$	-237.26 kcal/mol
$2Fe^{2+} + MnO_2(s) + 4H_2O = 2Fe(OH)_3(s) + 2H^+ + Mn^{2+}$	**-54.44 kJ/mol**

Solution at pH 6.5 containing 10^{-4} M Fe^{2+} and Mn^{2+} and both $Fe(OH)_3(s)$ and $MnO_2(s)$ present. **How will it Proceed?**

$$Q = \frac{\{Mn^{2+}\}\{H^+\}^2\{Fe(OH)_3(s)\}}{\{Fe^{2+}\}^2\{MnO_2(s)\}\{H_2O\}^4} = \frac{\{Mn^{2+}\}\{H^+\}^2}{\{Fe^{2+}\}^2}$$

$$= \frac{(10^{-4})(10^{-6.5})^2}{(10^{-4})^2} = 10^{-9}$$

$$\Delta G = \Delta G^0_{rxn} + RT\ln Q = -54.44 \text{ kJ/mol} + 2.47\ln(10^{-9})$$

= -105.6 kJ/mol

< 0 rxn proceed left to right

2nd Approach: Use Redox Potentials

E_{cell} = electrochemical version of ΔG for overall redox rxn

$$\Delta G = -nFE_{cell}$$

Potential (volts)

Faraday's Constant (96.485 kJ/V eq)

# of electrons transferred

$$\Delta G^0 = -nFE^0_{cell}$$

Direction	**ΔG**	**E_{cell}**
Rxn Proceed →	< 0	> 0
Equilibrium	0	0
Rxn Proceed ←	> 0	< 0

Power of approach is that E^0 tables available for ½ rxns

Conceptual & Practical Basis for E^0_{cell}

- In well mixed solution, oxidant & reductant are in close contact
  - Direct e^- transfer occurs
  - $2S_2O_3^{2-} + I_2 = S_4O_6^{2-} + 2I^-$
- Consider each ½ rxn in isolation
- Electrochemical Cell
  - Separate $S_2O_3^{2-}$ and I_2 into separate containers
  - Connect wire between cells (and include salt bridge) and current flows between cells
  - $S_2O_3^{2-}$ oxidized in left cell
  - I_2 reduced in right cell
  - $E^0_{cell} = E^0_{(RHR)} - E^0_{(OHR)}$ (S.T.P.)

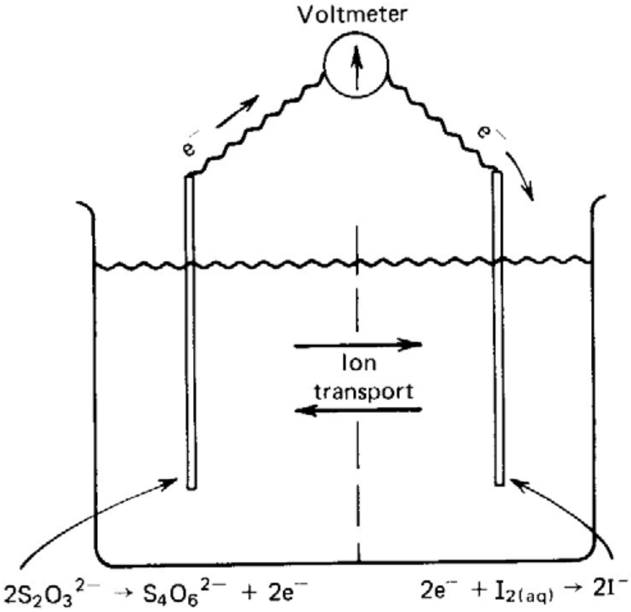


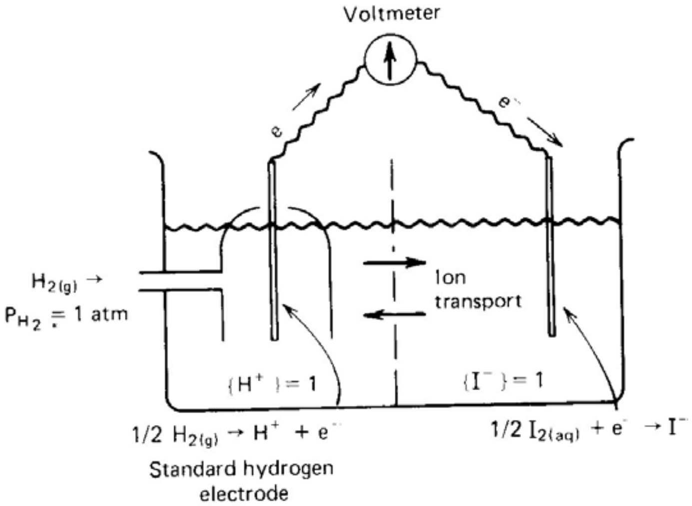
Fig. 7-1. Iodine-thiosulfate cell.

Conceptual & Practical Basis for E^0_{cell}

- E^0 values for half cells can't be determined absolutely
- E^0 values measured relative to reference cell assigned $E^0 = 0$ Volts at 1 atm and 298K (so measure E^0_{cell} where $E^0_{OHR} = 0$)
- Standard (or normal) hydrogen electrode:

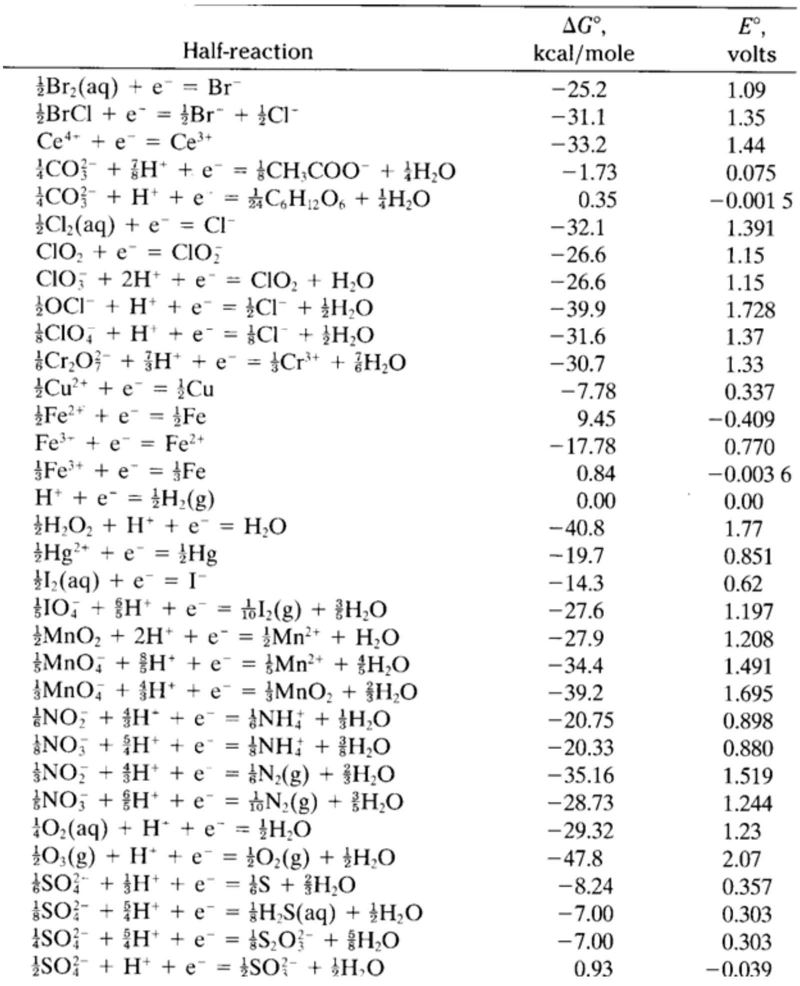
$$H^+ + e^- = \tfrac{1}{2}H_2(g) \qquad E^0 = 0 \text{ Volts} \quad \Delta G^0 \text{ also} = 0$$

- E^0 = ½ cell reduction potentials measured relative to NHE (V vs. NHE) (*NHE serves as OHR*)
- "+" value indicates stronger oxidant than H^+ & weaker reductant than H_2



Std Reduction Potential (E^0)

- Convention: Tables show potential for ½ rxns in direction of reduction
- E^0(oxidation direction) = $-E^0$(reduction direction)
- E^0 ↑: red direction more energetically favorable & oxidation direction less favorable
  - Stronger oxidants have large E^0
  - Stronger reductants have lower E^0



Half-reaction	$\Delta G°$, kcal/mole	$E°$, volts
$\frac{1}{2}Br_2(aq) + e^- = Br^-$	−25.2	1.09
$\frac{1}{2}BrCl + e^- = \frac{1}{2}Br^- + \frac{1}{2}Cl^-$	−31.1	1.35
$Ce^{4+} + e^- = Ce^{3+}$	−33.2	1.44
$\frac{1}{4}CO_3^{2-} + \frac{7}{8}H^+ + e^- = \frac{1}{8}CH_3COO^- + \frac{1}{4}H_2O$	−1.73	0.075
$\frac{1}{4}CO_3^{2-} + H^+ + e^- = \frac{1}{24}C_6H_{12}O_6 + \frac{1}{4}H_2O$	0.35	−0.001 5
$\frac{1}{2}Cl_2(aq) + e^- = Cl^-$	−32.1	1.391
$ClO_2 + e^- = ClO_2^-$	−26.6	1.15
$ClO_3^- + 2H^+ + e^- = ClO_2 + H_2O$	−26.6	1.15
$\frac{1}{2}OCl^- + H^+ + e^- = \frac{1}{2}Cl^- + \frac{1}{2}H_2O$	−39.9	1.728
$\frac{1}{8}ClO_4^- + H^+ + e^- = \frac{1}{8}Cl^- + \frac{1}{2}H_2O$	−31.6	1.37
$\frac{1}{6}Cr_2O_7^{2-} + \frac{7}{3}H^+ + e^- = \frac{1}{3}Cr^{3+} + \frac{7}{6}H_2O$	−30.7	1.33
$\frac{1}{2}Cu^{2+} + e^- = \frac{1}{2}Cu$	−7.78	0.337
$\frac{1}{2}Fe^{2+} + e^- = \frac{1}{2}Fe$	9.45	−0.409
$Fe^{3+} + e^- = Fe^{2+}$	−17.78	0.770
$\frac{1}{3}Fe^{3+} + e^- = \frac{1}{3}Fe$	0.84	−0.003 6
$H^+ + e^- = \frac{1}{2}H_2(g)$	0.00	0.00
$\frac{1}{2}H_2O_2 + H^+ + e^- = H_2O$	−40.8	1.77
$\frac{1}{2}Hg^{2+} + e^- = \frac{1}{2}Hg$	−19.7	0.851
$\frac{1}{2}I_2(aq) + e^- = I^-$	−14.3	0.62
$\frac{1}{5}IO_4^- + \frac{6}{5}H^+ + e^- = \frac{1}{10}I_2(g) + \frac{3}{5}H_2O$	−27.6	1.197
$\frac{1}{2}MnO_2 + 2H^+ + e^- = \frac{1}{2}Mn^{2+} + H_2O$	−27.9	1.208
$\frac{1}{5}MnO_4^- + \frac{8}{5}H^+ + e^- = \frac{1}{5}Mn^{2+} + \frac{4}{5}H_2O$	−34.4	1.491
$\frac{1}{3}MnO_4^- + \frac{4}{3}H^+ + e^- = \frac{1}{3}MnO_2 + \frac{2}{3}H_2O$	−39.2	1.695
$\frac{1}{6}NO_2^- + \frac{4}{3}H^+ + e^- = \frac{1}{6}NH_4^+ + \frac{1}{3}H_2O$	−20.75	0.898
$\frac{1}{8}NO_3^- + \frac{5}{4}H^+ + e^- = \frac{1}{8}NH_4^+ + \frac{3}{8}H_2O$	−20.33	0.880
$\frac{1}{3}NO_2^- + \frac{4}{3}H^+ + e^- = \frac{1}{6}N_2(g) + \frac{2}{3}H_2O$	−35.16	1.519
$\frac{1}{5}NO_3^- + \frac{6}{5}H^+ + e^- = \frac{1}{10}N_2(g) + \frac{3}{5}H_2O$	−28.73	1.244
$\frac{1}{4}O_2(aq) + H^+ + e^- = \frac{1}{2}H_2O$	−29.32	1.23
$\frac{1}{2}O_3(g) + H^+ + e^- = \frac{1}{2}O_2(g) + \frac{1}{2}H_2O$	−47.8	2.07
$\frac{1}{6}SO_4^{2-} + \frac{1}{3}H^+ + e^- = \frac{1}{6}S + \frac{2}{3}H_2O$	−8.24	0.357
$\frac{1}{8}SO_4^{2-} + \frac{5}{4}H^+ + e^- = \frac{1}{8}H_2S(aq) + \frac{1}{2}H_2O$	−7.00	0.303
$\frac{1}{4}SO_4^{2-} + \frac{5}{4}H^+ + e^- = \frac{1}{8}S_2O_3^{2-} + \frac{5}{8}H_2O$	−7.00	0.303
$\frac{1}{2}SO_4^{2-} + H^+ + e^- = \frac{1}{2}SO_3^{2-} + \frac{1}{2}H_2O$	0.93	−0.039

Is a redox reaction favorable?

- $E^0_{cell} = E^0_{RHR} - E^0_{OHR}$
- Subtract the E^0 value of the ½ reaction that will be going in the opposite (oxidation) direction from the E^0 value of the ½ reaction that will be undergoing reduction
  - **Note:** Only works when adding 2 half reactions where 1 donates e^- and other accepts same number of e^-
- If $E^0_{cell} > 0$: favorable; < 0 unfavorable
  - Consider oxidation of Mn^{2+} by permanganate (MnO_4^-):

	E^0 (V vs. NHE)	ΔG^0 kJ mol^{-1}
$6 \times (H_2O + \frac{1}{2}Mn^{2+} = \frac{1}{2}MnO_2(s) + 2H^+ + e^-)$	1.21	$6\{-(-116.7)\} = +700.4$
$6 \times (e^- + 4/3\ H^+ + 1/3\ MnO_4^- = 1/3\ MnO_2(s) + 2/3H_2O)$	1.70	$6(-164) = -984.0$
$3Mn^{2+} + 2\ MnO_4^- + 2H_2O = 5MnO_2(s) + 4H^+$	+0.49 V	−283.7 kJ mol^{-1}

✓ **Reaction Favorable**

Caveat: only true for std state conditions (pH 0, 1 M conc., 25 ° C, 1 atm)

- Sometimes use tables of E_7^0 values (corrected to **pH 7**, 1 M conc., 25 ° C, 1 atm)

Nernst Equation:
Potentials at non-standard conditions

Recall: $\Delta G = \Delta G^0_{rxn} + RT \ln Q$ & $E = \dfrac{\Delta G}{-nF}$

It Follows:

$$\frac{\Delta G}{-nF} = \frac{\Delta G^0}{-nF} + \frac{RT}{-nF} \ln Q$$

Or

$$E = E^0 - \frac{RT}{nF} \ln Q$$

Also

$$E^0 = \frac{RT}{nF} \ln K_{eq}$$

Consider oxidation of Fe^{2+} by $MnO_{2(s)}$ again:

$2Fe^{2+} + MnO_2(s) + 4H_2O = 2Fe(OH)_3(s) + 2H^+ + Mn^{2+}$ **E^0_{cell} = 0.146 V**

$$E_{cell} = E^0{}_{cell} - \frac{RT}{nF} \ln Q$$

Solution at pH 6.5 containing 10^{-4} M Fe^{2+} and Mn^{2+} and both $Fe(OH)_3(s)$ and $MnO_2(s)$ present. **How will rxn Proceed?**

$$Q = \frac{\{Mn^{2+}\}\{H^+\}^2\{Fe(OH)_3(s)\}}{\{Fe^{2+}\}^2\{MnO_2(s)\}\{H_2O\}^4} = \frac{\{Mn^{2+}\}\{H^+\}^2}{\{Fe^{2+}\}^2}$$

$$= \frac{(10^{-4})(10^{-6.5})^2}{(10^{-4})^2} = 10^{-9}$$

$$E_{cell} = E^0{}_{cell} - \frac{RT}{nF} \ln Q$$ = 0.146 – 0.0128lnQ

= +0.411 Volts

> 0 rxn proceed left to right

- Can make Nernst Eqn valid for ½ rxns by coupling with NHE

$$\begin{array}{lr} Cu^{2+} + e^- = Cu^+ & E^0 = +0.16 \text{ V vs. NHE} \\ \tfrac{1}{2}H_2(g) = H^+ + e^- & E^0 = 0 \text{ V vs. NHE} \\ \hline Cu^{2+} + \tfrac{1}{2}H_2(g) = Cu+ + H+ & E^0{}_{cell} = +0.16 \text{ V vs. NHE} \end{array}$$

$$E_{cell} = E^0{}_{cell} - \frac{RT}{nF}\ln Q = 0.16 - \frac{RT}{nF}\ln\frac{\{Cu^+\}\{H^+\}}{\{Cu^{2+}\}P_{H_2}{}^{0.5}}$$

- In NHE side: $E^0 = 0$, $\{H^+\} = 1$ and $P_{H2} = 1$ atm, so all terms drop out of Nernst expression. Therefore

$$E = E^0 - \frac{RT}{nF}\ln\frac{\{Cu^+\}}{\{Cu^{2+}\}}$$

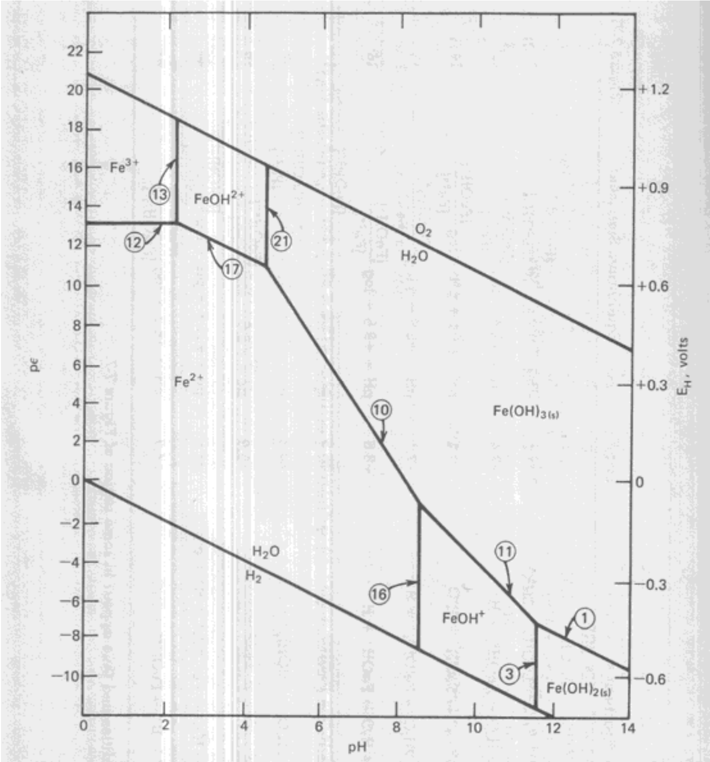
Clarify

- **E** for ½ rxns tells us potential relative to $H_2(g)/H^+$ redox couple
- **E_{cell}** for overall reaction indicates whether rxn is at equilibrium or not (<0, 0, or >0)

Nernst Eqn

- Effect of reactant and product concentration
  - Evaluate equilibrium position
    - When $E_{cell} = 0$ or when $E_{(RHR)} = E_{(OHR)}$
- Assess how system conditions like pH affect half reaction potentials
  - Does Fe^{2+} become stronger reductant as we increase system pH?

Predominance Area Diagrams (E-pH)



- Areas represent pH-E conditions where a particular Fe(II) or Fe(III) species “predominates” over all other Fe(II) & Fe(III) species

- Lines represent boundaries where 2 “predominant” species are equal

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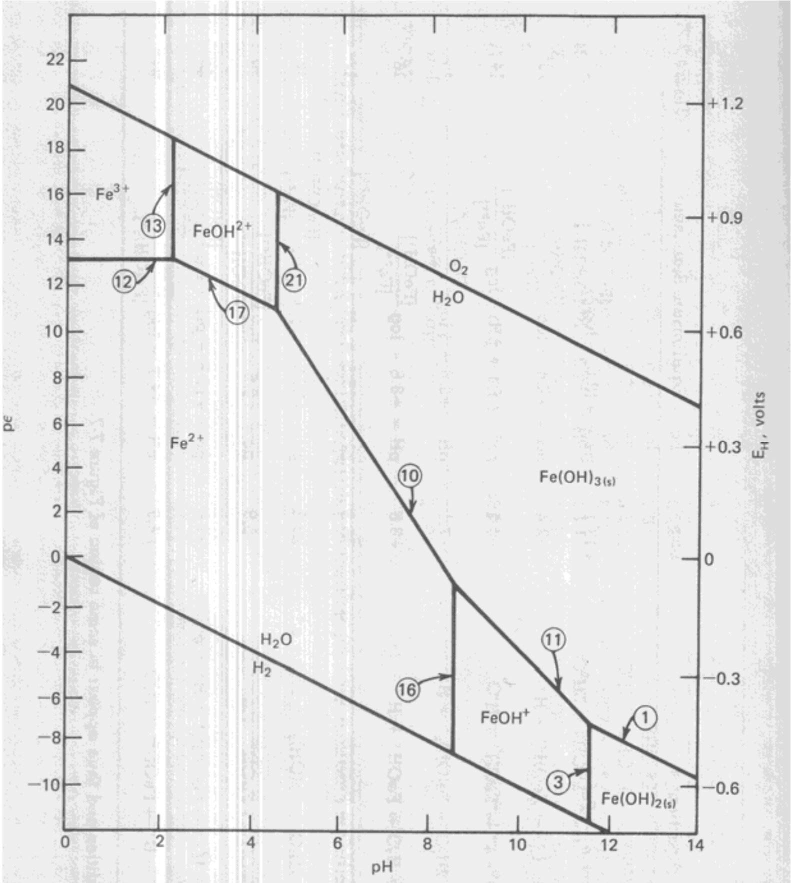
How are predominance diagrams useful?

- If you are given the pH and E values (e.g., measured by pH and redox probes) of a given environment, you can estimate which species predominates
  - i.e., [i] $\approx C_T$ (or is present if the predominant species is a solid)
  - Simplifies calculating remainder of reactant/product species
  - 1) use Ka, β, etc… to calculate concentration of other species from the same oxidation state as the predominant species.
  - 2) use Nernst equation to then calculate the concentration of one species of the other oxidation state at the E-pH condition
  - 3) use Ka, β, etc… to calculate concentration of other species from the 2nd oxidation state.

E-pH Diagram for 10^{-7} M Iron



(1) pH = 5, E = +0.1 V

(2) pH = 8.5, E = +0.3 V

(3) pH = 8.5, E = -0.3 V

What about the $H_2O/O_{2(g)}$ and $H_2O/H_{2(g)}$ lines?

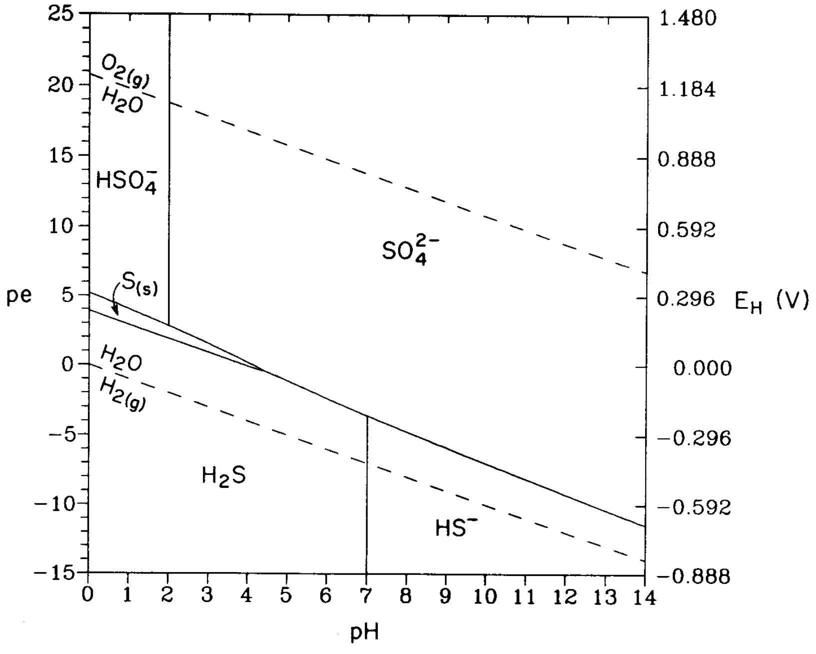


Figure 23.12 pe-pH diagram for aqueous sulfur when $S_T = 10^{-3}$ *M* and 25°C/1 atm. Activity corrections are neglected. $S_{(s)}$ is only possible at relatively low pH. As the pe is lowered at any given pH value, the diagram indicates that S(−II) (either as H_2S or as HS^-) can become the dominant form of sulfur before the in-situ p_{H_2} can reach 1 atm.

What about the $H_2O/O_{2(g)}$ and $H_2O/H_{2(g)}$ lines?

- Represent the thermodynamic stability limits of H_2O
- If system $E > E_{H2O/O2}$ line, water should get oxidized to $O_{2(g)}$

$$2H_2O = 4H^+ + 4e^- + O_{2(g)} \quad E^0 = 1.226\ V$$

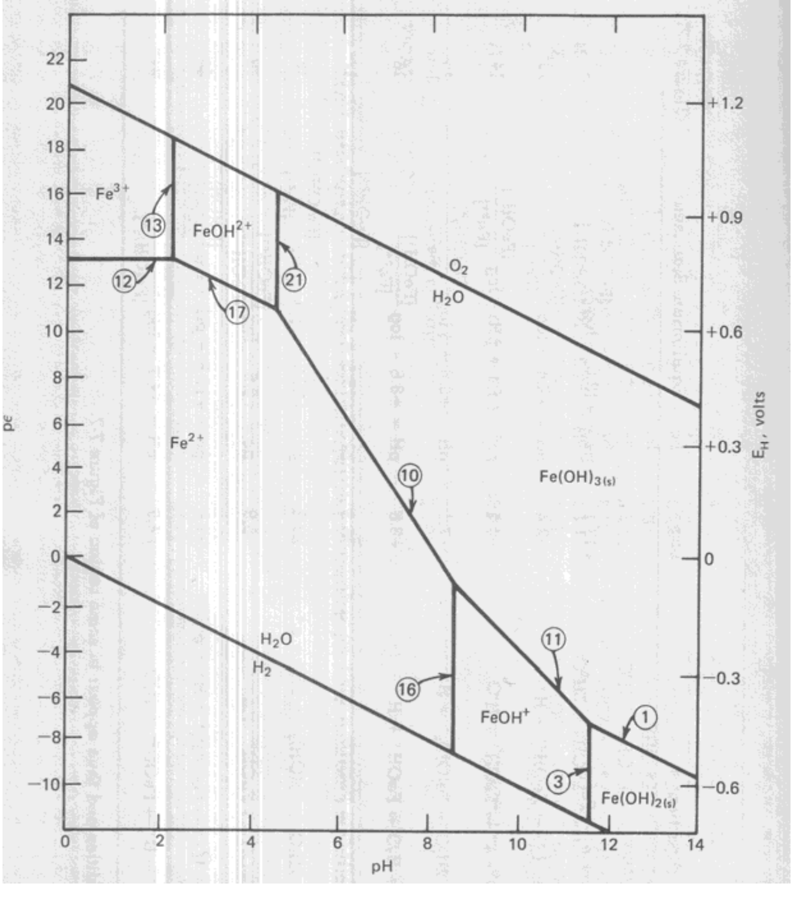
$$E = 1.226 - \left(\frac{0.0256}{4}\right)\ln\left(\frac{\{H_2O\}^2}{\{O_{2(g)}\}\{H^+\}^4}\right)$$

- If system $E < E_{H2O/H2}$ line, water should get reduced to $H_{2(g)}$

$$2H^+ + 2e^- = H_{2(g)} \quad E^0 = 0.0\ V$$

$$E = 0 - \left(\frac{0.0256}{2}\right)\ln\left(\frac{\{H_{2(g)}\}}{\{H^+\}^2}\right)$$

E-pH Diagram for 10^{-7} M Iron



(1) pH = 5, E = +0.1 V

(4) Now, imagine that this groundwater is pumped from the ground and equilibrated with the atmosphere where E is buffered by the H_2O/O_2 redox couple.

Recalculate iron speciation