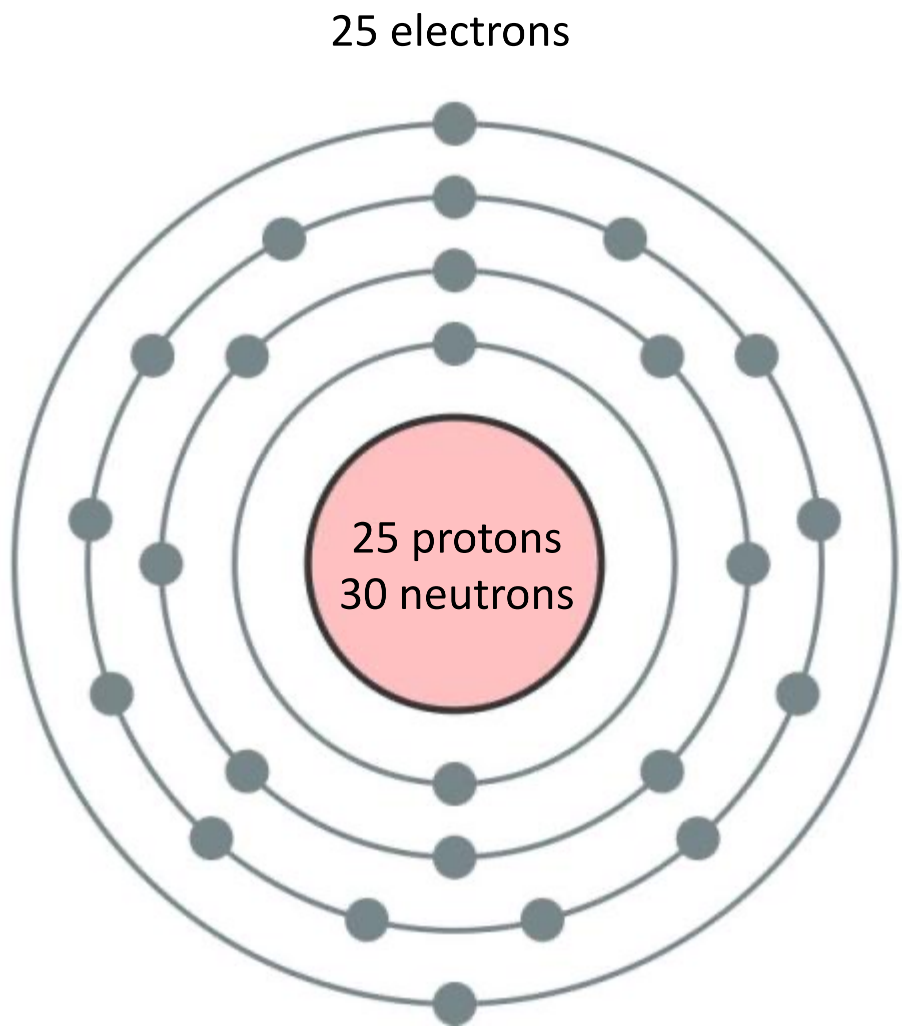
REDOX REACTIONS

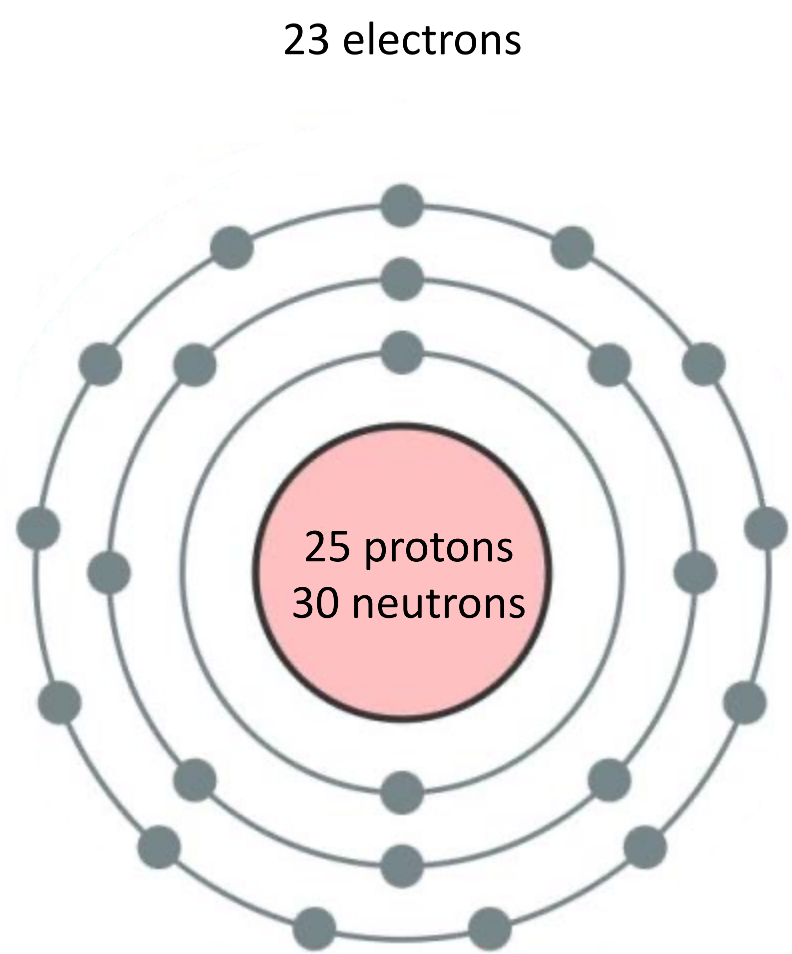
EAR 419/619 Aqueous Geochemistry

Elements lose and gain electrons to form different ***oxidation states***



Metallic Mn – equal number of protons (+) and electrons (-)
Oxidation state = 0

Elements lose and gain electrons to form different *oxidation states*

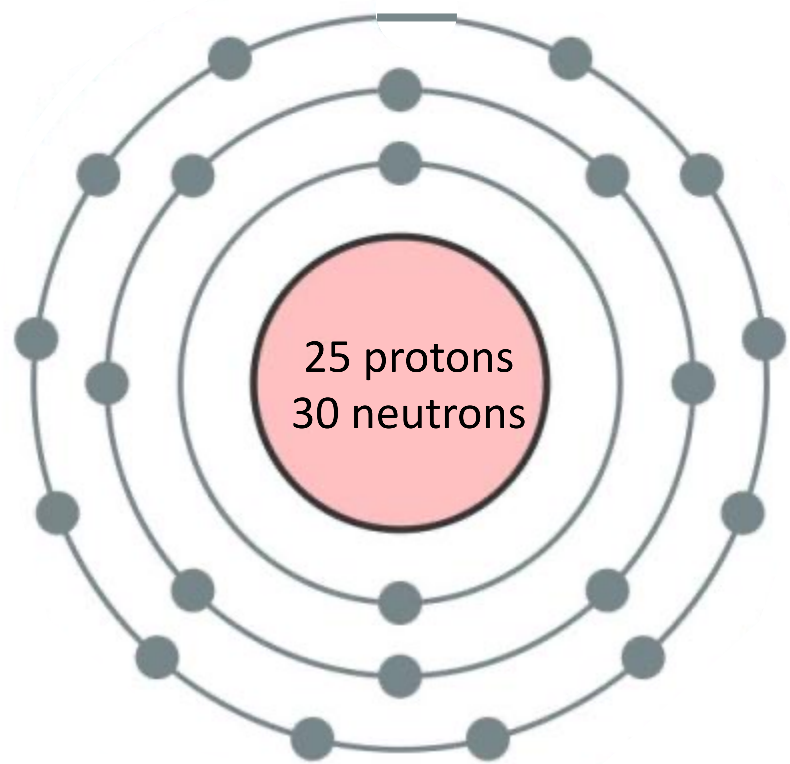


Mn^{2+} – gives up 2 electrons to create charge deficit

Oxidation state = +2

Elements lose and gain electrons to form different ***oxidation states***

22 electrons

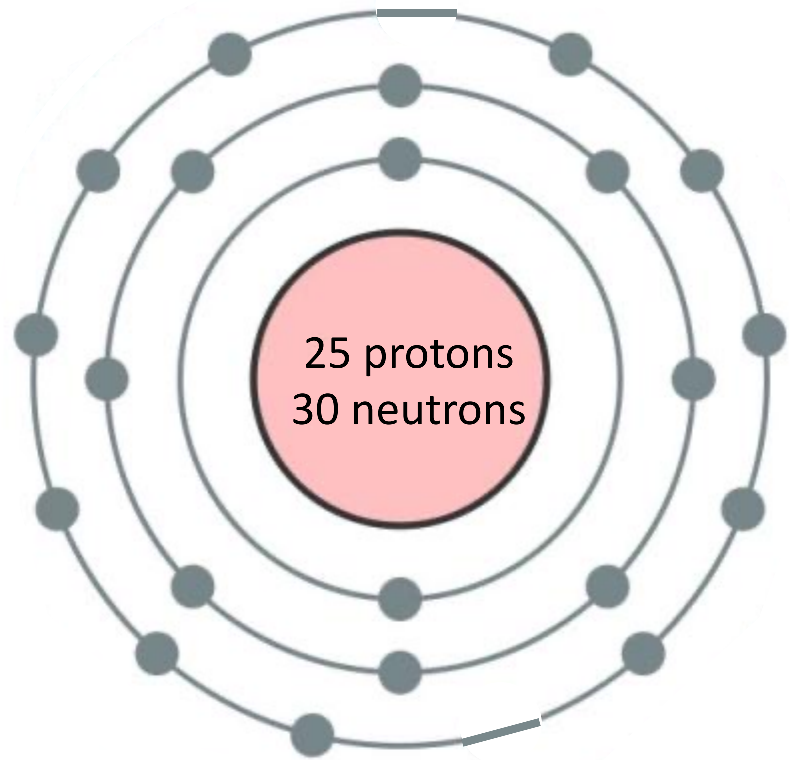


Mn^{3+} – gives up 3 electrons to create charge deficit

Oxidation state = +3

Elements lose and gain electrons to form different ***oxidation states***

21 electrons



Mn^{4+} – gives up 4 electrons to create charge deficit

Oxidation state = +4

Rules for determining the oxidation state of an element in a compound:

1. An element bonded to itself has an oxidation state of zero (supercedes the other rules)
2. Hydrogen (H) is always +1
3. Oxygen (O) is always -2
4. The sum of the oxidation states of all elements in the compound must add up to the total charge on the compound

Examples: O_2 gas, CO_2, CH_4, CH_2O (organic matter), SeO_4^{2-}

Redox (oxidation – reduction) reactions

Definition: Transfer of electrons from the electron donor (reducing agent) to the electron acceptor (oxidizing agent)

Oxidation

Is

Loss of electrons

Reduction

Is

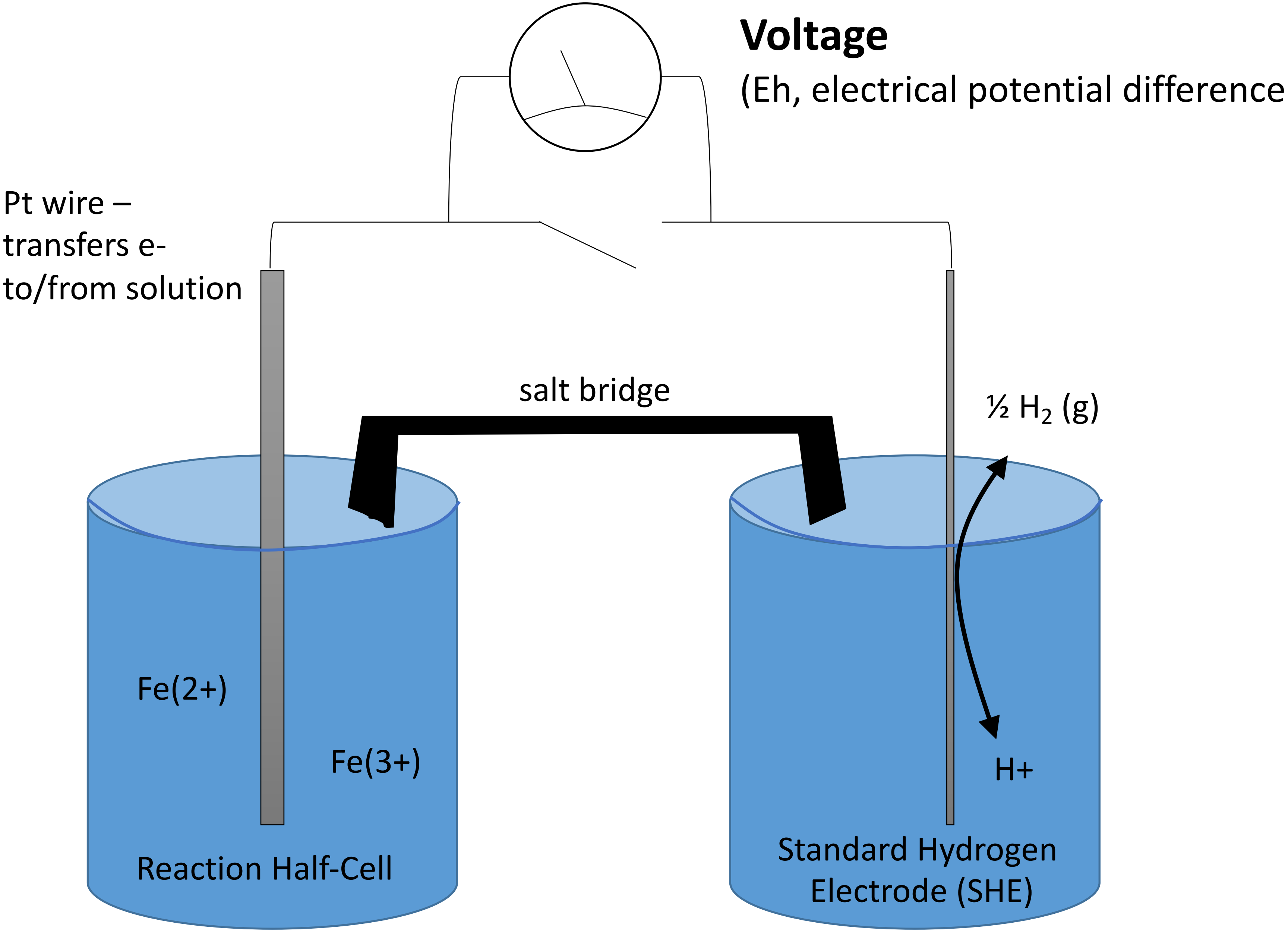
Gain of electrons

Oxidation:

$A^0 \rightarrow A^+ + e^-$

Reduction:

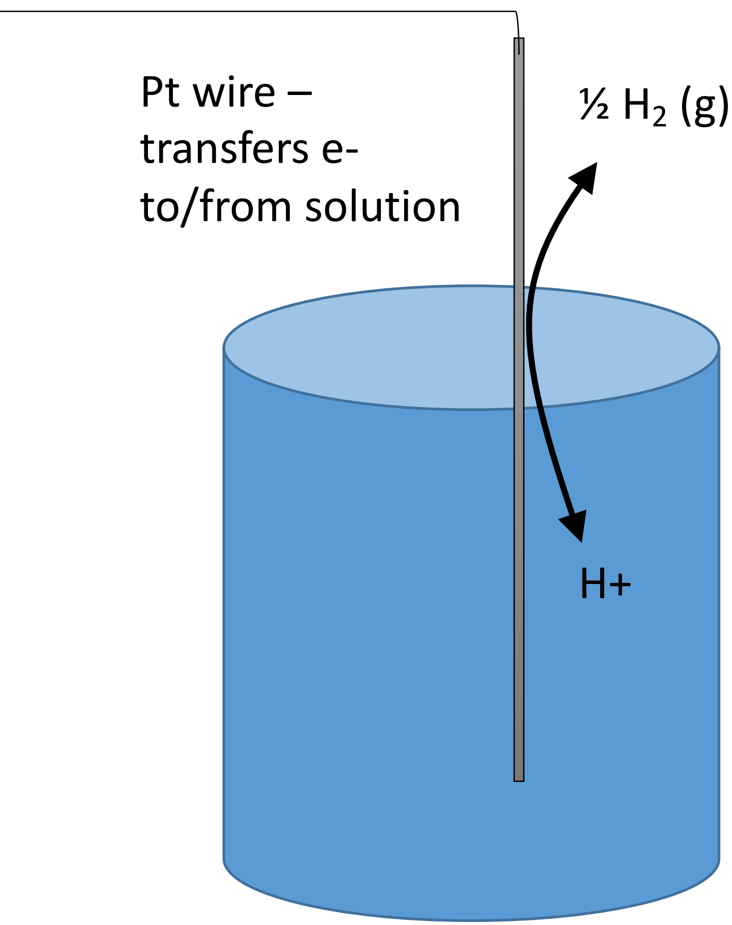
$B^+ + e^- \rightarrow B^0$



ELECTROCHEMICAL CELL

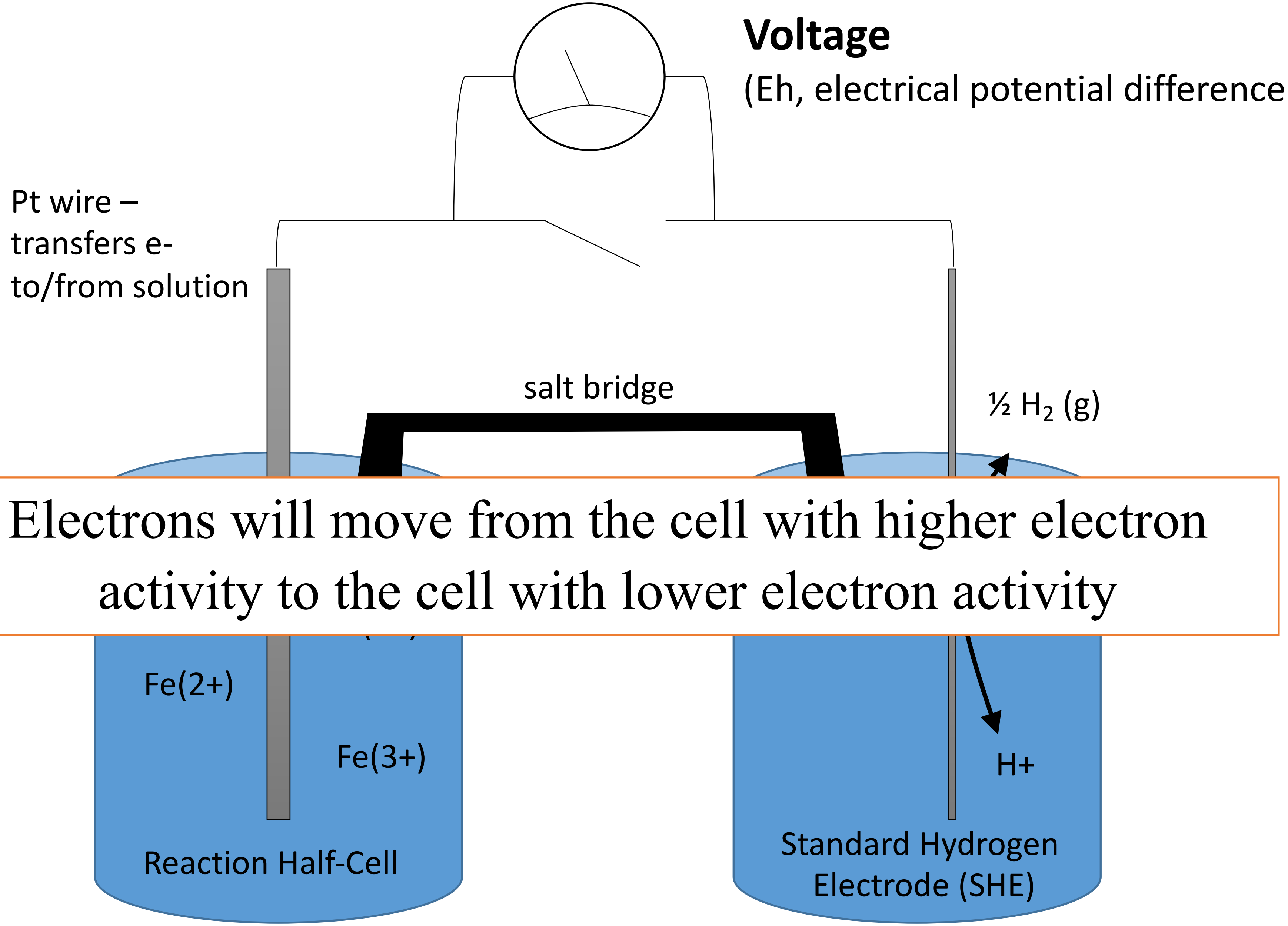
STANDARD HYDROGEN ELECTRODE (SHE)

the redox reference state



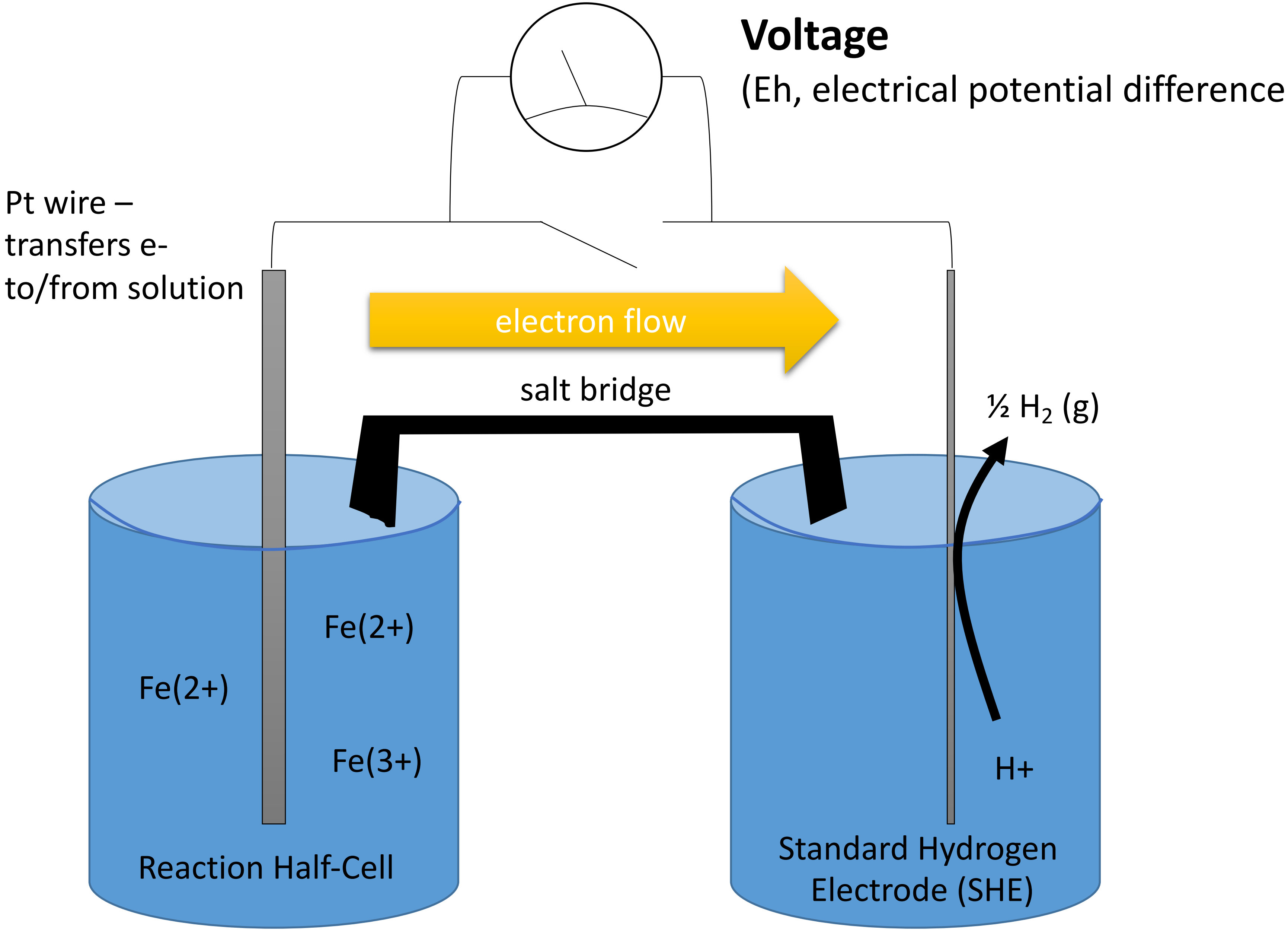
SHE half-cell

- The electric potential of a half-reaction is determined relative to a reference state (SHE)
- The H_2/H+ half-reaction at 25°C with P_{H2} = 1 atm and a_{H+} = 1
- Electric potential of SHE = 0 *by convention*

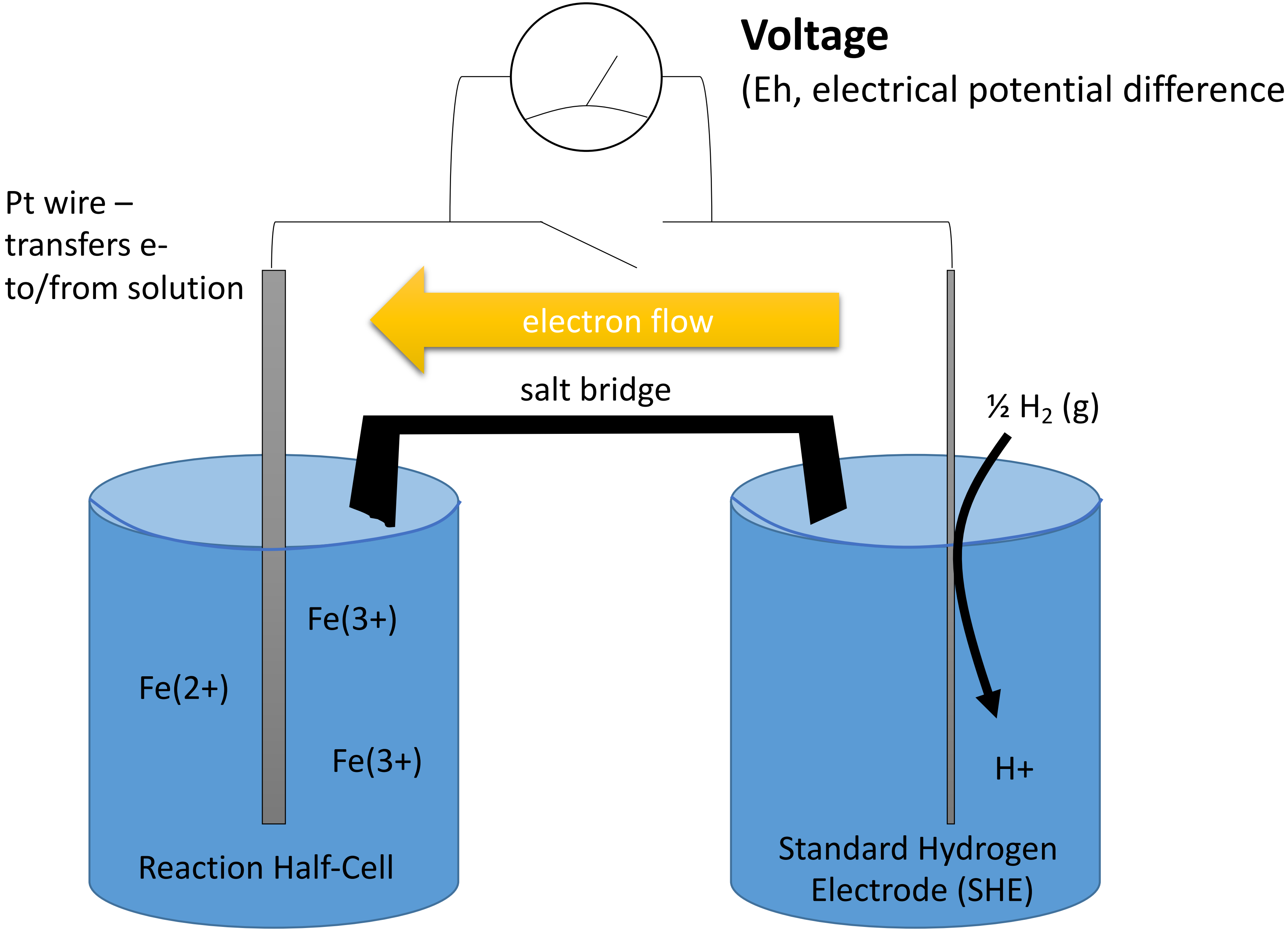


Electrons will move from the cell with higher electron activity to the cell with lower electron activity

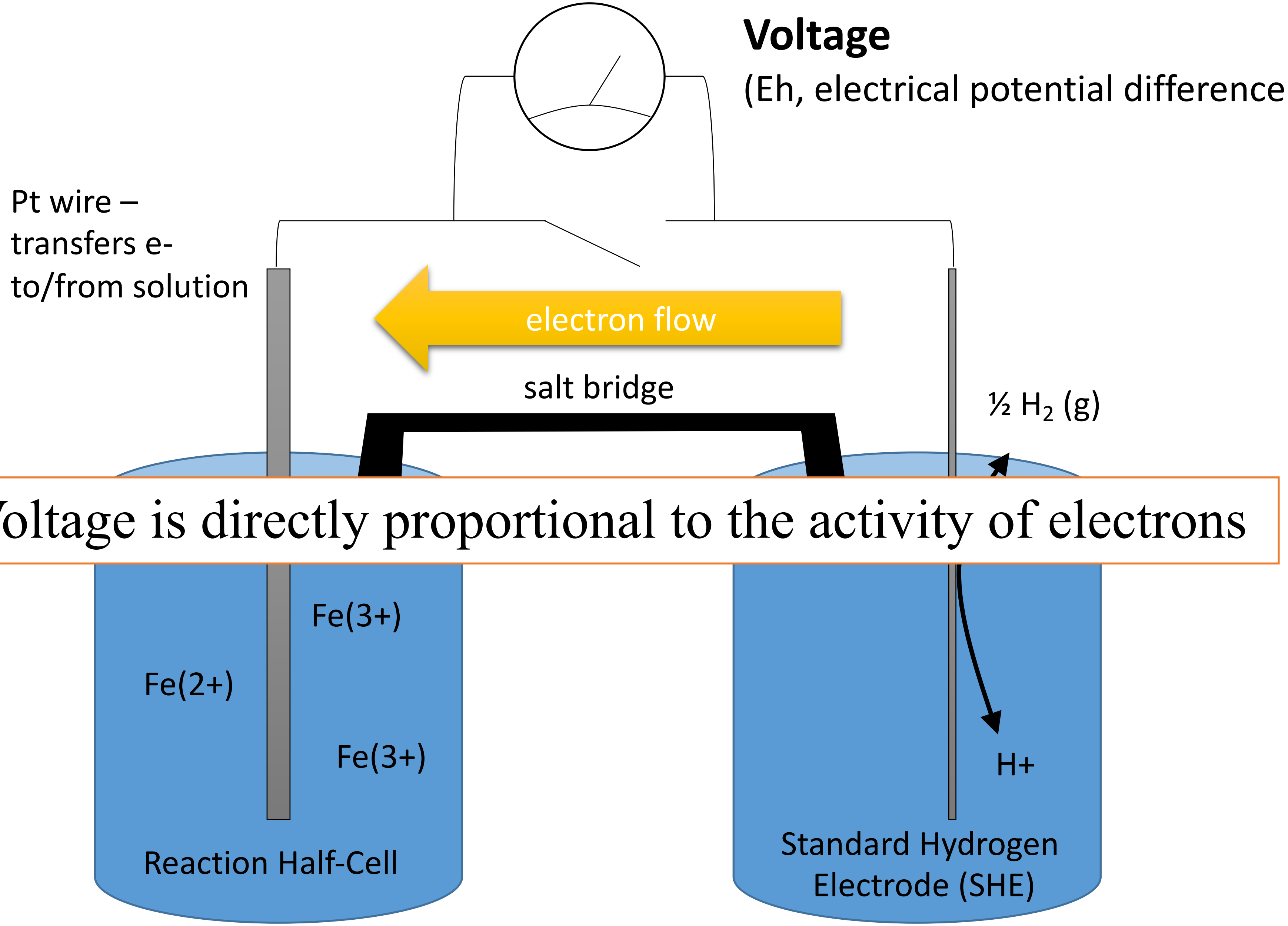
ELECTROCHEMICAL CELL



ELECTROCHEMICAL CELL



ELECTROCHEMICAL CELL



Voltage is directly proportional to the activity of electrons

ELECTROCHEMICAL CELL

Redox Potential of Common Redox Rxn.

- The energy generated from a reaction (ΔG) depends on the difference in reduction potential between the e- donor and acceptor
- If $E^0 > 0$, then the half-reaction is favorable
  - Reactant easily accepts e- to be reduced
  - High reduction potential
- If $E^0 < 0$, then the half-reaction is unfavorable
  - Reaction would rather proceed in the opposite direction
  - that is, the product would rather give up its electrons

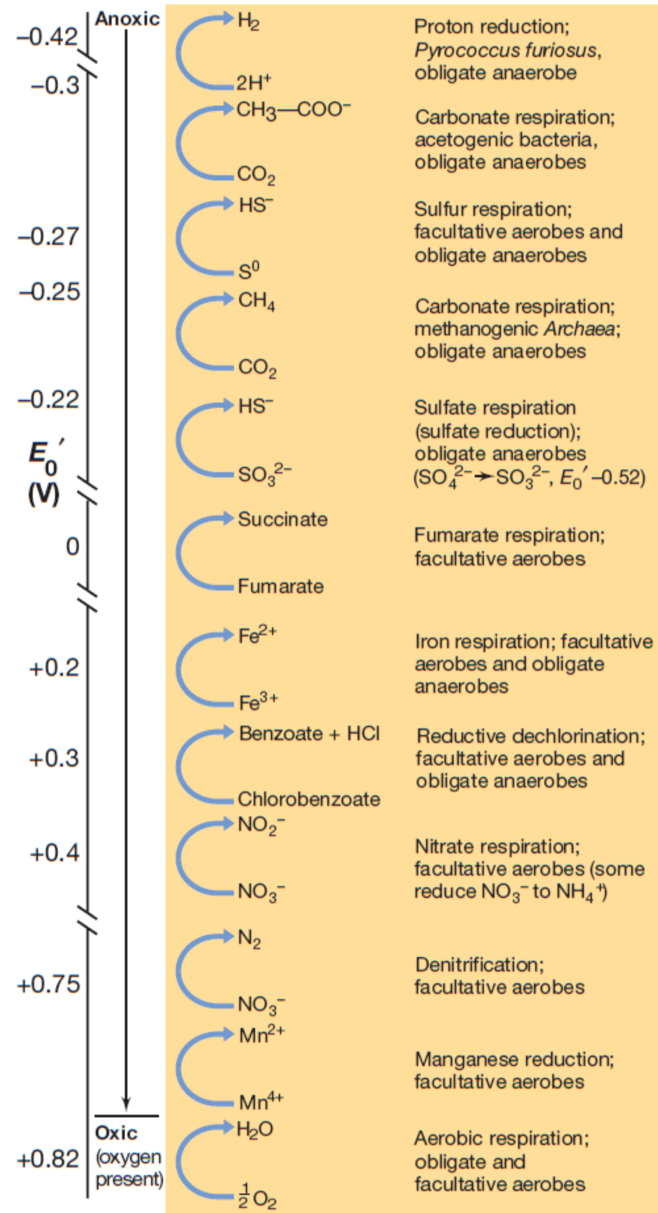
Reaction	E°(V)
$Ag^+ + e^- = Ag^0_{(s)}$	0.797
$Al^{3+} + 3e^- = Al^0_{(s)}$	−1.686
$AsO_4^{3-} + 2H^+ + 2e^- = AsO_3^{3-} + H_2O$	0.156
$HOBr + H^+ + 2e^- = Br^- + H_2O$	1.338
$2HOBr + 2H^+ + 2e^- = Br_{2(aq)} + 2H_2O$	1.581
$BrO_3^- + 6H^+ + 6e^- = Br^- + 3H_2O$	1.437
$CO_{2(g)} + 8H^+ + 8e^- = CH_{4(g)} + 2H_2O$	0.170
$6CO_{2(g)} + 24H^+ + 24e^- = \text{glucose} + 6H_2O$	−0.012
$CO_{2(g)} + 4H^+ + 4e^- = CH_2O + H_2O$	−0.071
$CO_{2(g)} + H^+ + 2e^- = HCOO^-$	−0.285
$CH_2O + 2H^+ + 2e^- = CH_3OH$	0.236
$CH_2O + 4H^+ + 4e^- = CH_{4(g)} + H_2O$	0.410
$CH_3OH + 2H^+ + 2e^- = CH_{4(g)} + H_2O$	0.584
$Cl_{2(aq)} + 2e^- = Cl^-$	1.392
$HOCl + H^+ + 2e^- = Cl^- + H_2O$	1.481
$ClO_2 + 4H^+ + 5e^- = Cl^- + 2H_2O$	1.495
$ClO_2^- + 4H^+ + 4e^- = Cl^- + 2H_2O$	1.609
$ClO_3^- + 6H^+ + 6e^- = Cl^- + 3H_2O$	1.446
$Co^{3+} + e^- = Co^{2+}$	1.953
$CrO_4^{2-} + 8H^+ + 3e^- = Cr^{3+} + 4H_2O$	1.514
$Cu^{2+} + e^- = Cu^+$	0.160
$Cu^{2+} + 2e^- = Cu^0_{(s)}$	0.339
$Fe^{3+} + e^- = Fe^{2+}$	0.769
$Fe^{2+} + 2e^- = Fe^0_{(s)}$	−0.441
$2H^+ + 2e^- = H_{2(g)}$	0.000
$2H^+ + 2e^- = H_{2(aq)}$	−0.092
$2Hg^{2+} + 2e^- = Hg_2^{2+}$	0.908
$Hg_2^{2+} + e^- = 2Hg_{(l)}$	0.794
$MnO_4^- + 8H^+ + 5e^- = Mn^{2+} + 4H_2O$	1.508
$MnO_{2(s)} + 4H^+ + 2e^- = Mn^{2+} + 2H_2O$	1.227
$Mn^{3+} + e^- = Mn^{2+}$	1.505
$Ni^{2+} + 2e^- = Ni^0_{(s)}$	−0.236
$O_{2(g)} + 4H^+ + 4e^- = 2H_2O$	1.226
$O_{2(aq)} + 4H^+ + 4e^- = 2H_2O$	1.268
$O_{2(aq)} + 2H^+ + 2e^- = H_2O_{2(aq)}$	0.777
$H_2O_{2(aq)} + 2H^+ + 2e^- = 2H_2O$	1.758
$Pb^{4+} + 2e^- = Pb^{2+}$	0.845
$Pb^{2+} + 2e^- = Pb^0_{(s)}$	−0.126
$SO_4^{2-} + 10H^+ + 8e^- = H_2S_{(aq)} + 4H_2O$	0.299
$SO_4^{2-} + 9H^+ + 8e^- = HS^- + 4H_2O$	0.248
$SO_4^{2-} + 2H^+ + 2e^- = SO_3^{2-} + H_2O$	0.801
$SeO_4^{2-} + 4H^+ + 2e^- = H_2SeO_3 + H_2O$	1.071
$Zn^{2+} + 2e^- = Zn^0_{(s)}$	−0.760

The Redox Ladder in Biology

- The energy generated from a reaction (ΔG) depends on the difference in reduction potential between the e- donor and acceptor

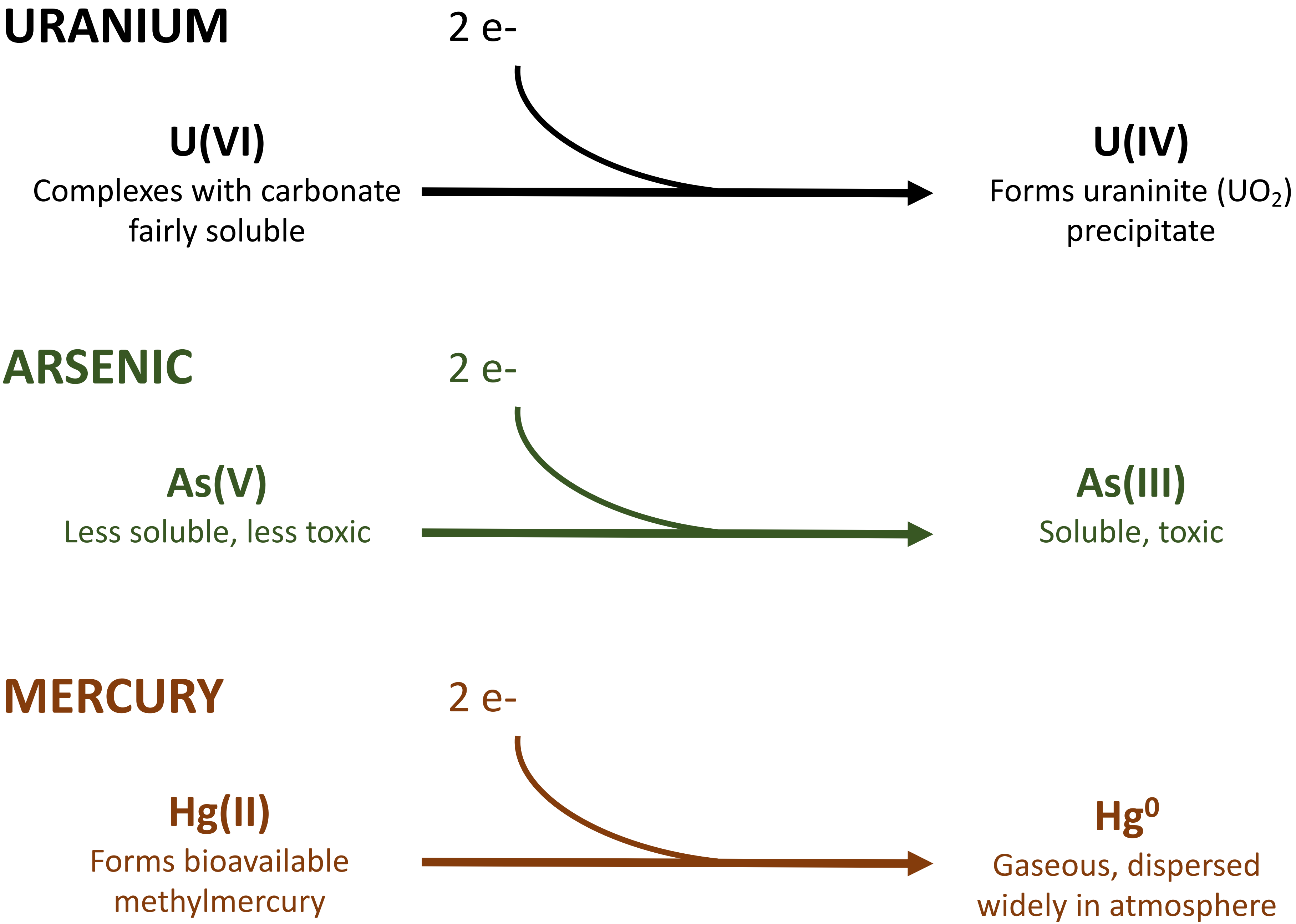
- If $E^0 > 0$, then the half-reaction is favorable
    - Reactant easily accepts e- to be reduced
    - High reduction potential

- If $E^0 < 0$, then the half-reaction is unfavorable
    - Reaction would rather proceed in the opposite direction
    - that is, the product would rather give up its electrons



Redox reactions in the environment

Image by Ohio DNR



URANIUM
2 e-
U(VI)
Complexes with carbonate
fairly soluble
U(IV)
Forms uraninite (UO_2)
precipitate
ARSENIC
2 e-
As(V)
Less soluble, less toxic
As(III)
Soluble, toxic
MERCURY
2 e-
Hg(II)
Forms bioavailable
methylmercury
Hg^0
Gaseous, dispersed
widely in atmosphere

URANIUM

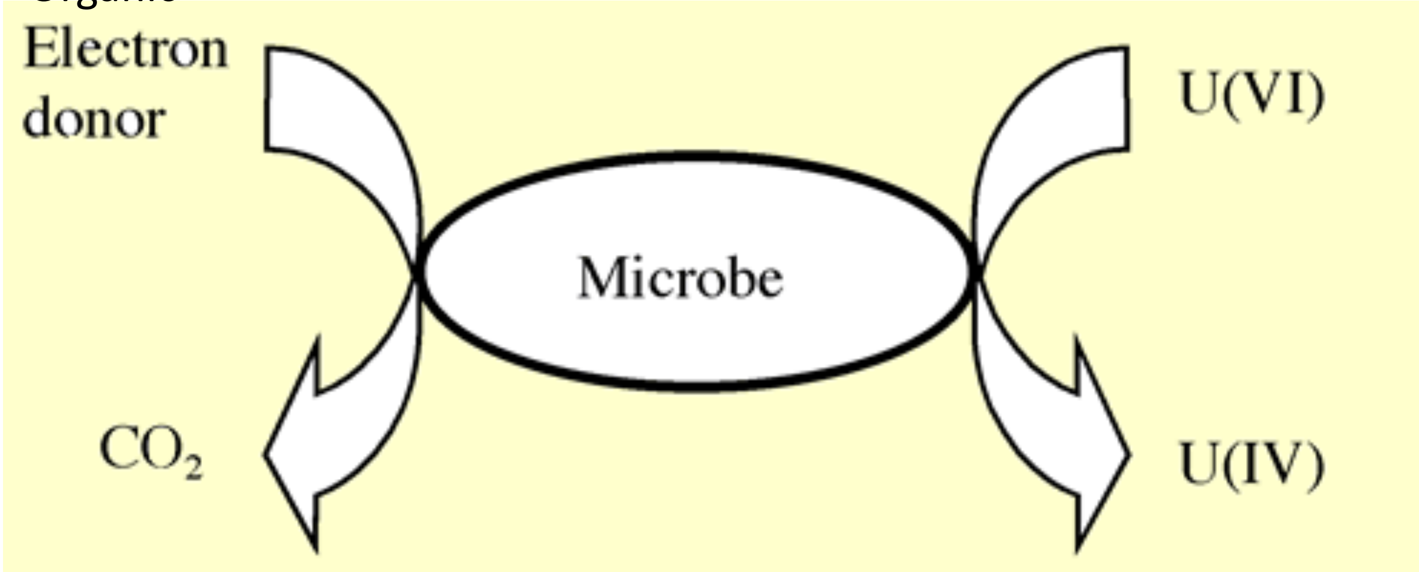
2 e-

U(VI) → **U(IV)**

U(VI)
Complexes with carbonate
fairly soluble

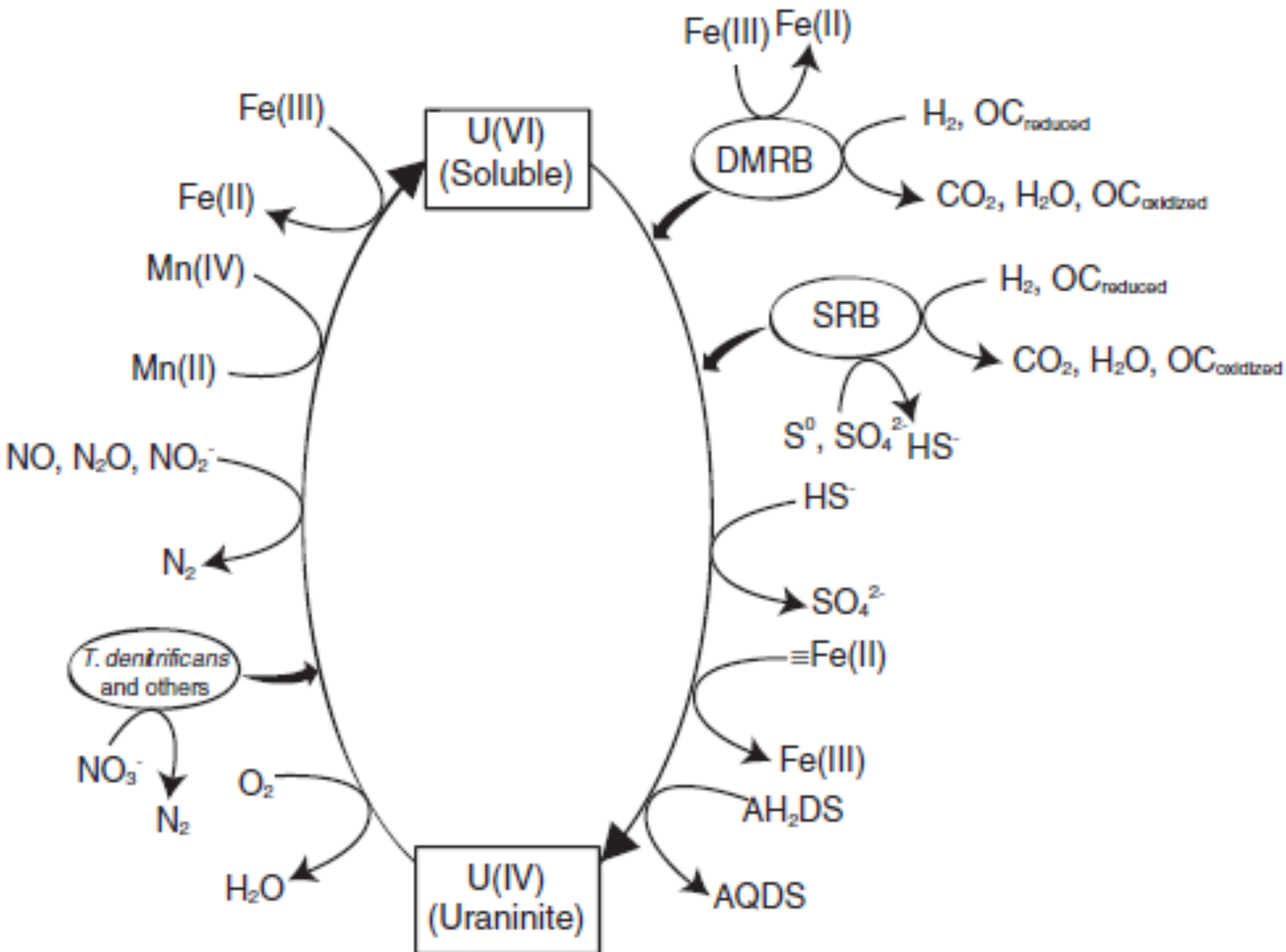
U(IV)
Forms uraninite (UO_2)
precipitate

Organic



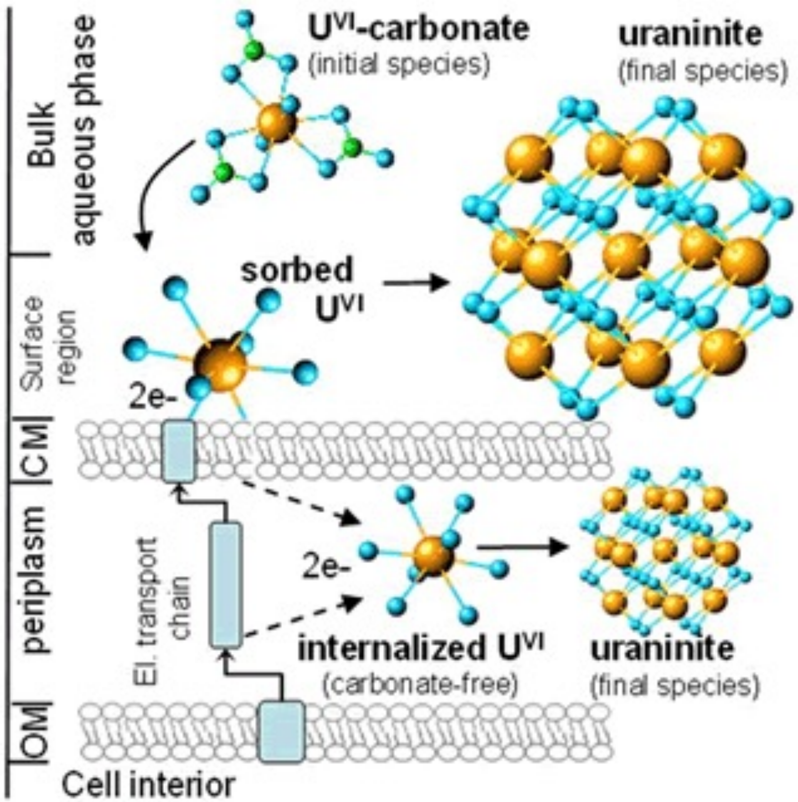
stanford.edu

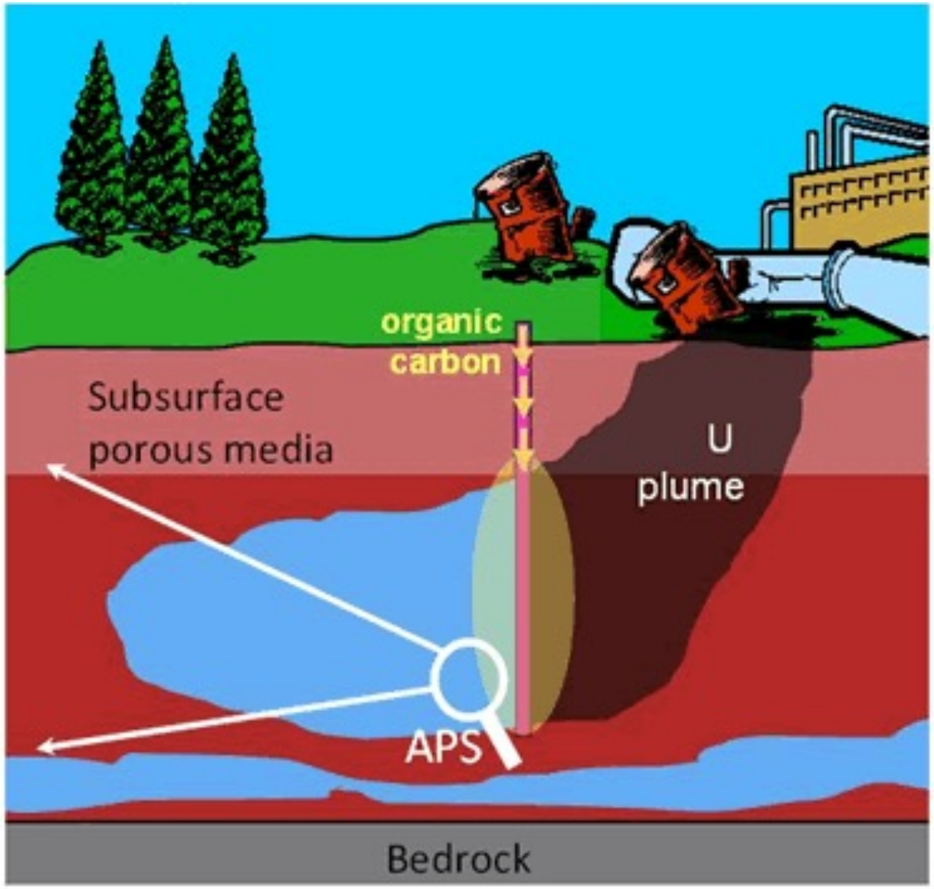
Various redox-active species can oxidize or reduce Uranium



Ginder-Vogel and Fendorf (2008)

Utilizing U redox to mitigate groundwater spills





www.bio.anl.gov

ARSENIC

2 e-

As(V)

Arsenate – AsO_4^{3-}

Less soluble, less toxic

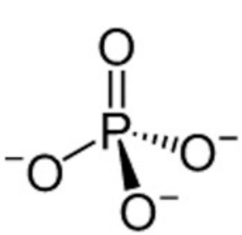
LD_{50} = 20 – 800 mg/kg

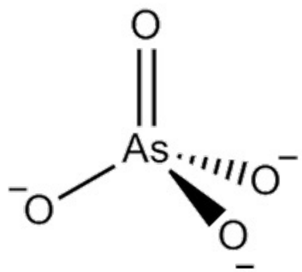
As(III)

Arsenite – AsO_3^{3-}

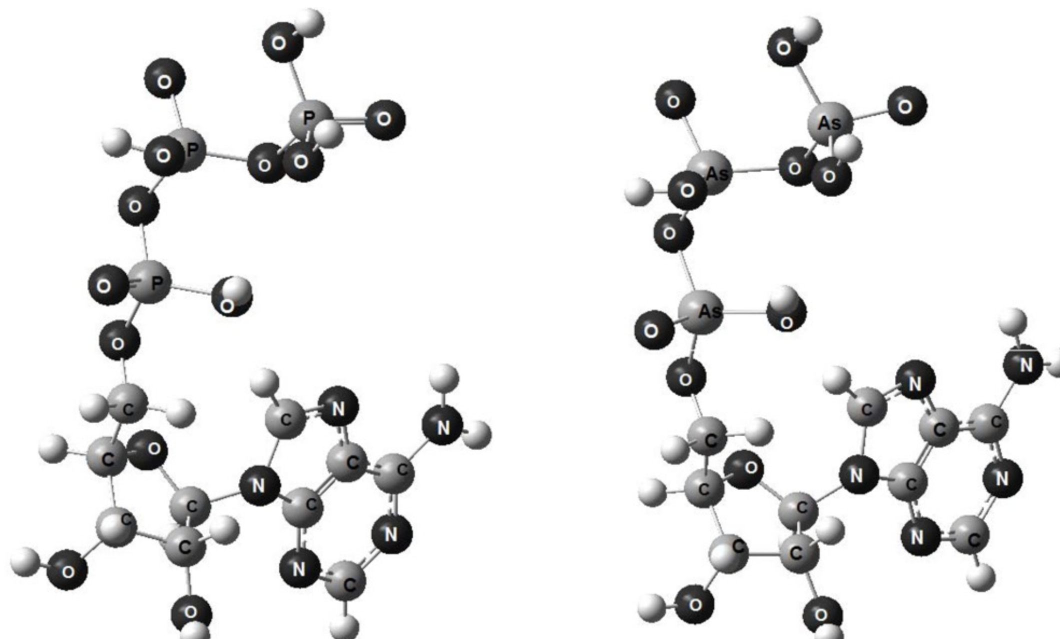
More soluble, more toxic

LD_{50} = 15 – 42 mg/kg





Adenosine triphosphate (ATP)

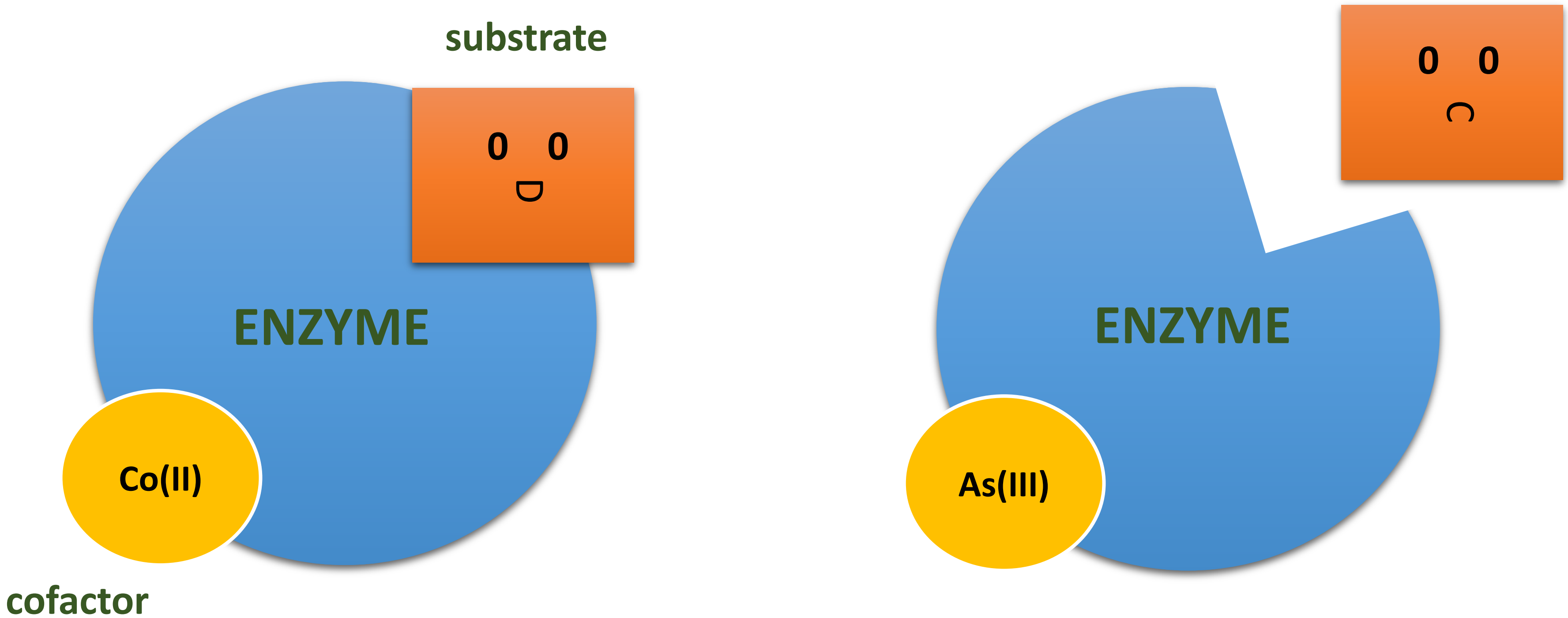


(a) (b)

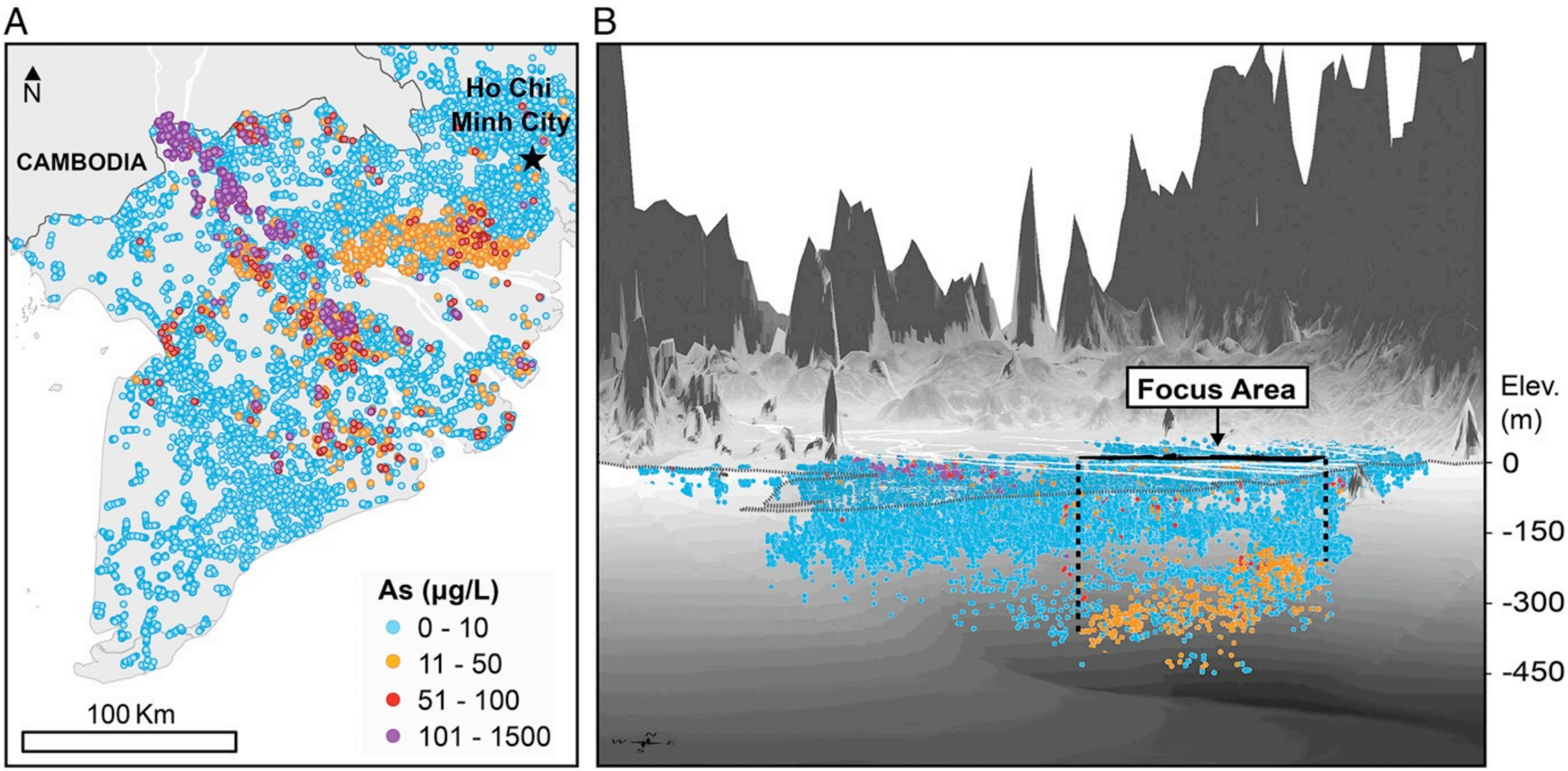
ARSENIC

As(V) $\xrightarrow{2\ e^-}$ **As(III)**

As(V)	As(III)
Arsenate – AsO_4^{3-}	Arsenite – AsO_3^{3-}
Less soluble, less toxic	More soluble, more toxic
LD_{50} = 20 – 800 mg/kg	LD_{50} = 15 – 42 mg/kg



Arsenic contamination in groundwater in southeast Asia is a major health concern

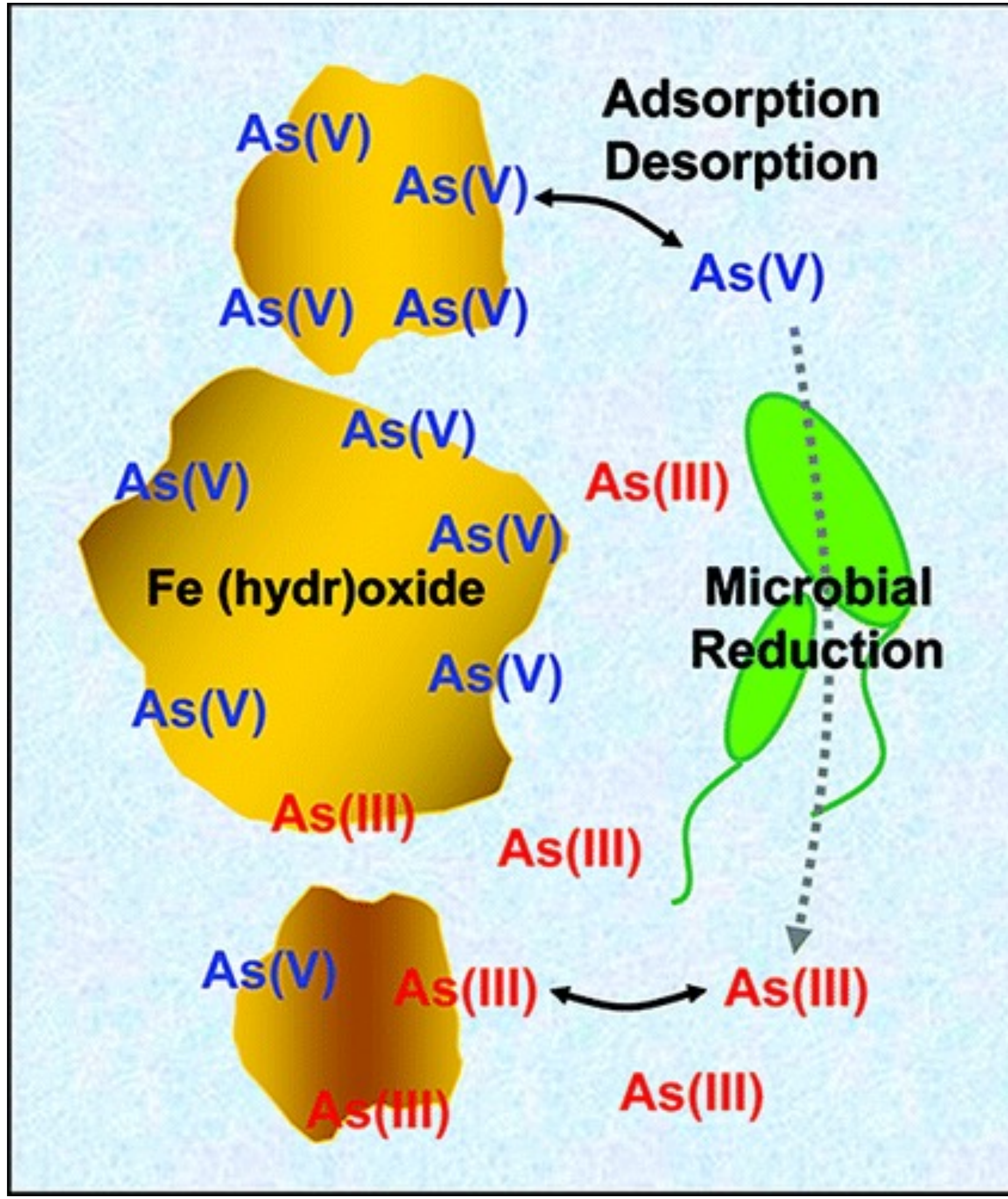


USEPA: As < 10 ug/L

Erban et al. 2013 PNAS

Redox reactions impact As mobility

- As(V) binds strongly to Fe-oxides at low to neutral pH
- Microbes can reduce As(V) to As(III) and release it into solution



Huang et al. (2011) ES&T

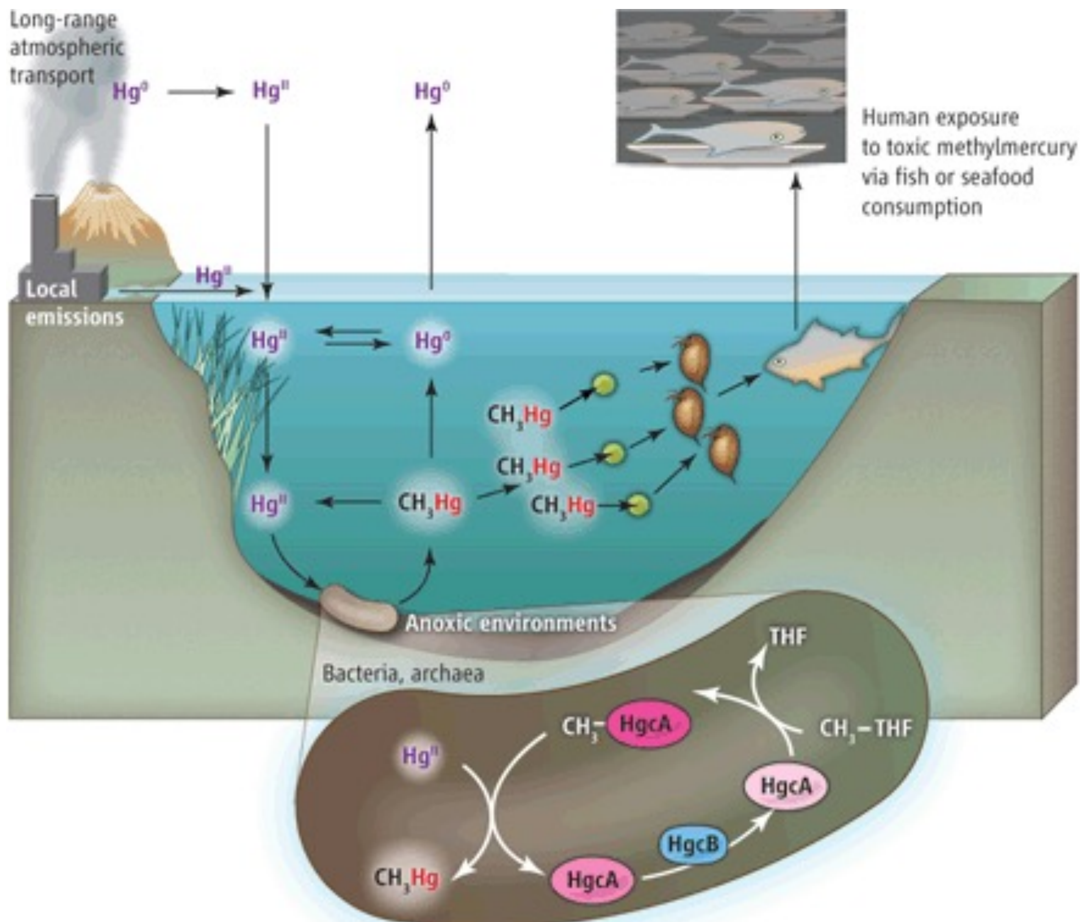
MERCURY

2 e-

Hg(II)
Forms bioavailable methylmercury

Hg^0
Gaseous, dispersed widely in atmosphere

Fossil fuel combustion contributed ~66% of anthropogenic global Hg emission (mostly from coal) in 2000

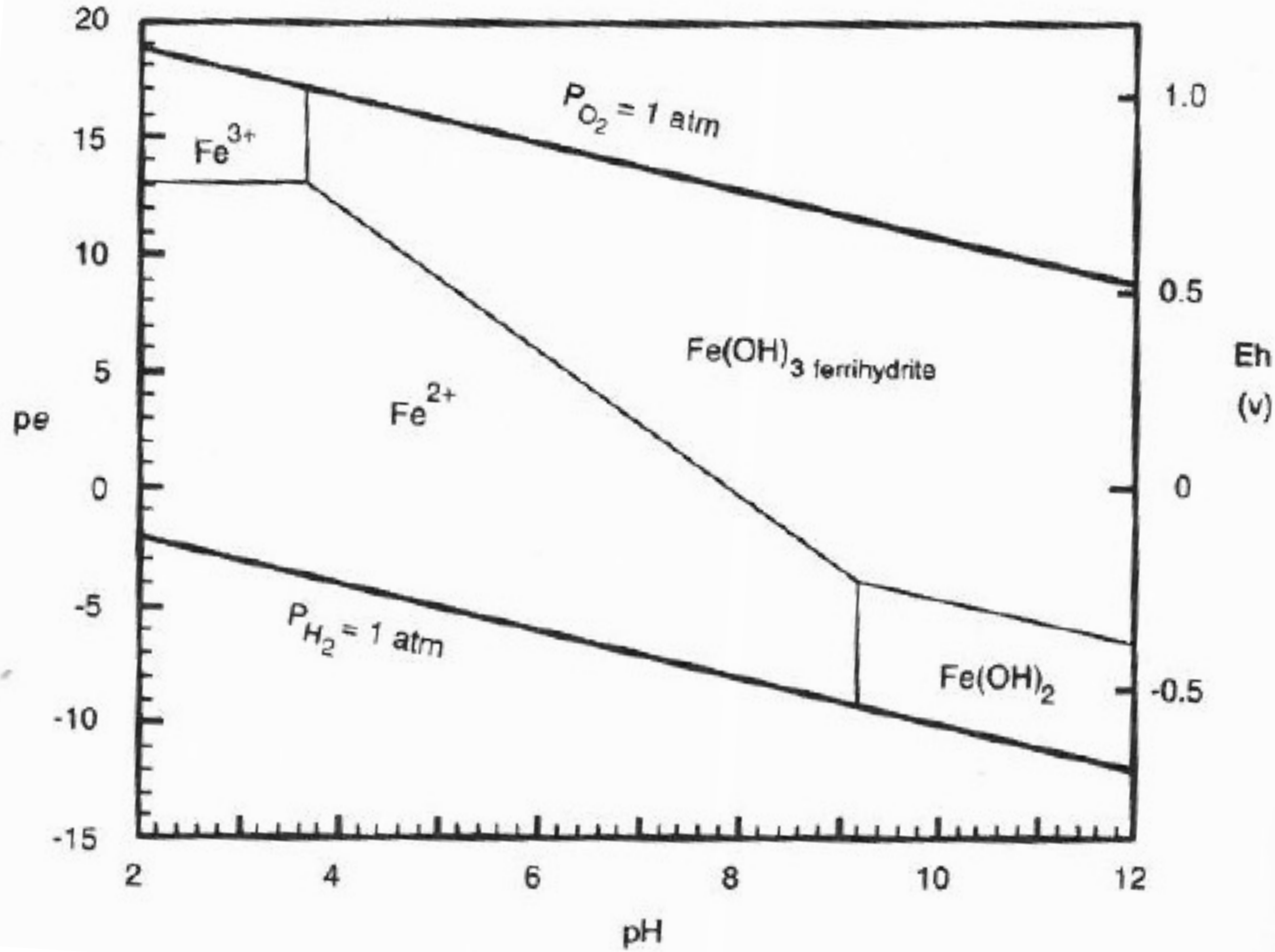


Poulain and Barkay (2013)

Eh-pH diagrams

- constructed using thermodynamic data
- predict the most stable form of an element for a **given system** under certain Eh and pH conditions
- Changes from one species to another represent redox or acid-base reactions

Under what conditions does Fe precipitate as $Fe(OH)_3$?



Fe-O-H_2O system at 25°C with ferrihydrite and $Fe(OH)_2$ as the iron oxide phases

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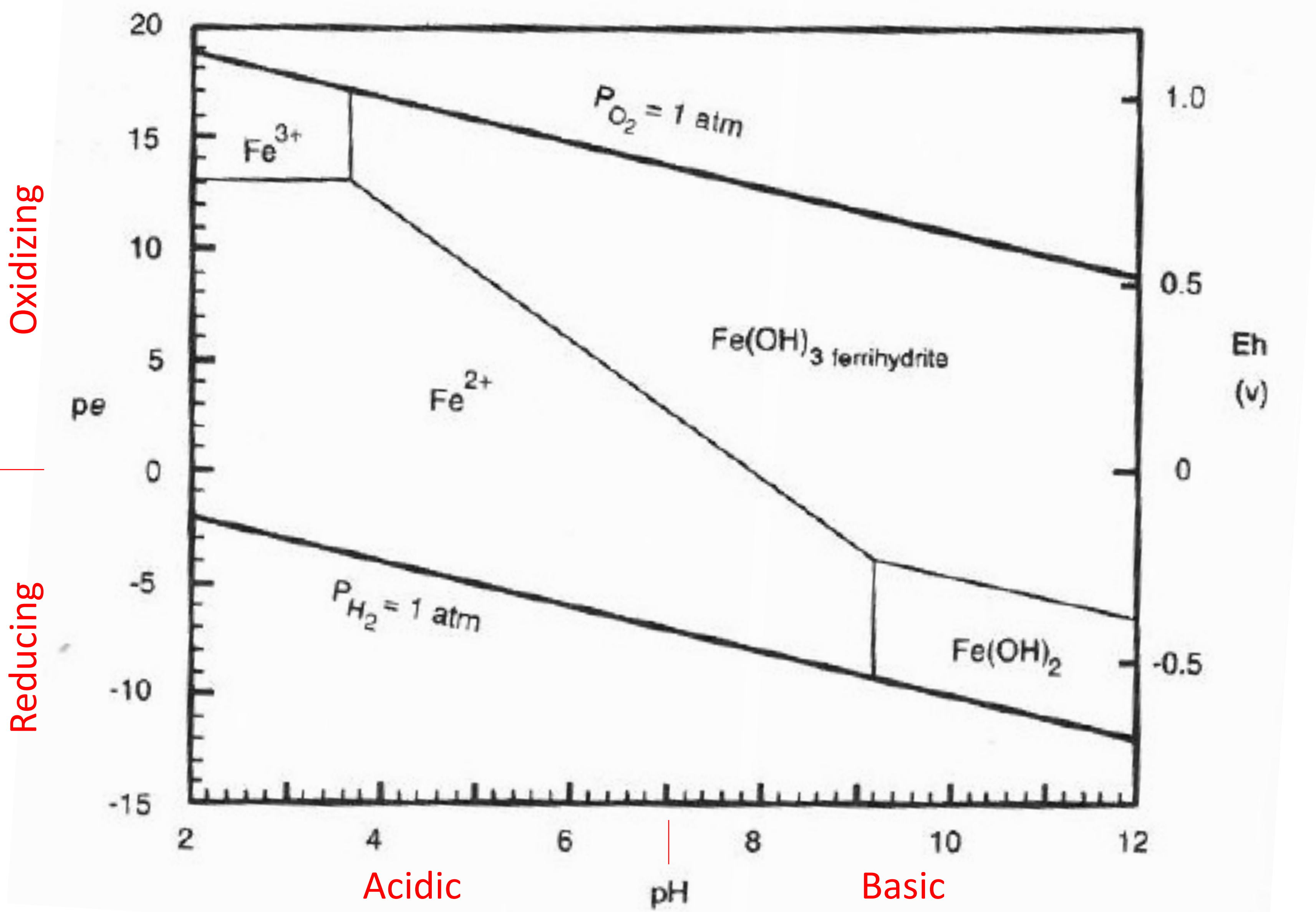

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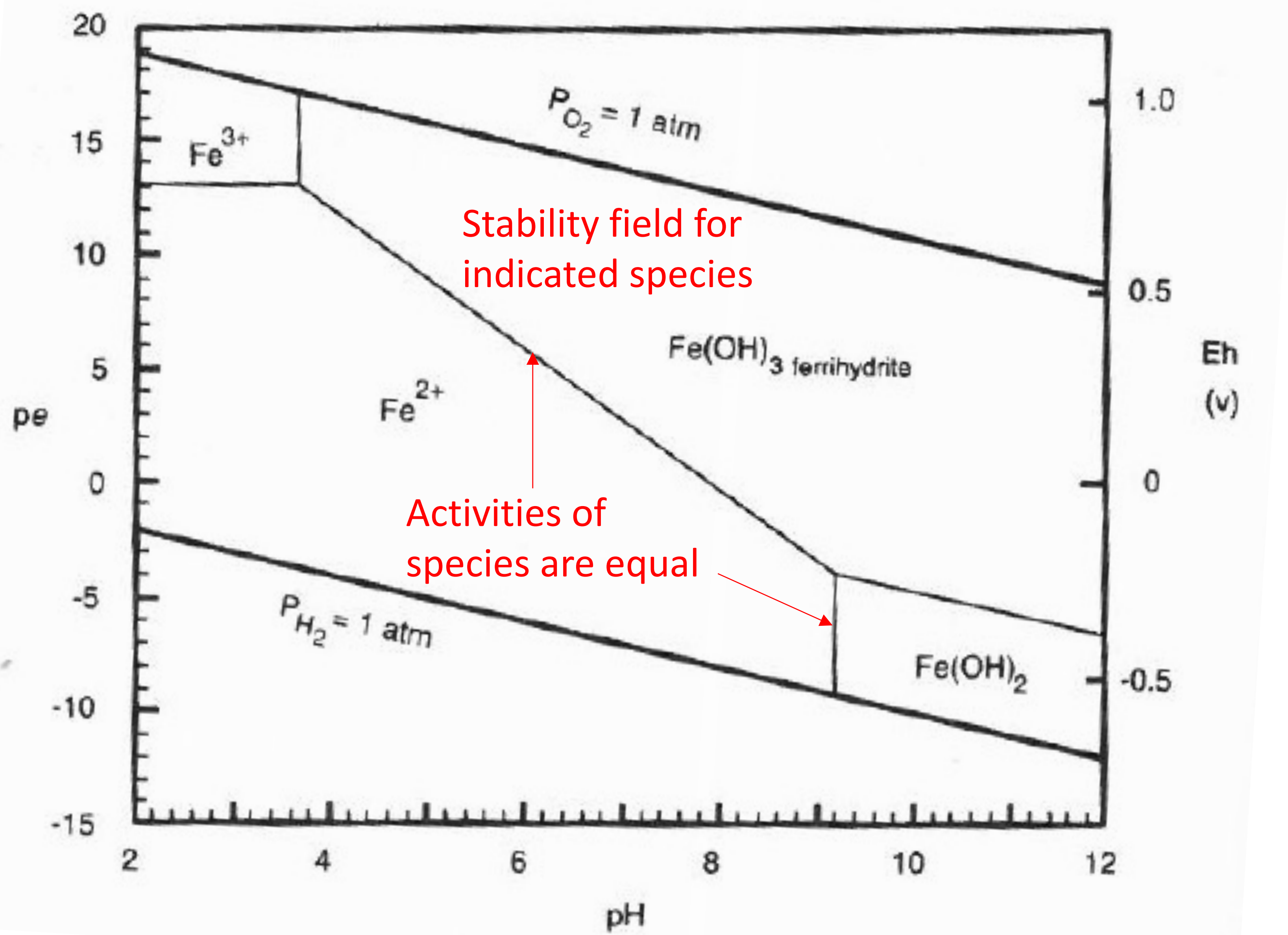

$Fe\text{-}O\text{-}H_2O$ system at 25°C with ferrihydrite and $Fe(OH)_2$ as the iron oxide phases

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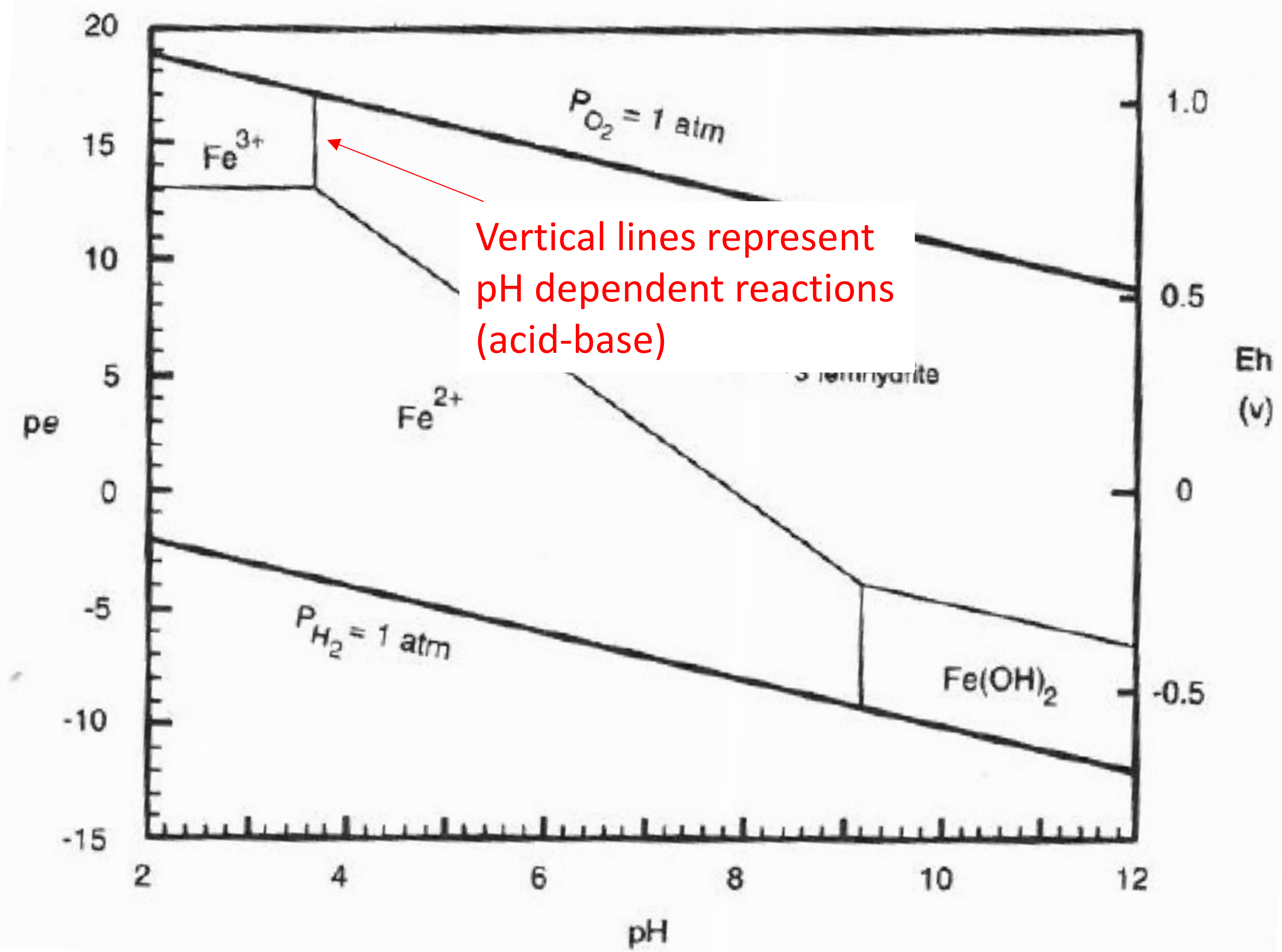

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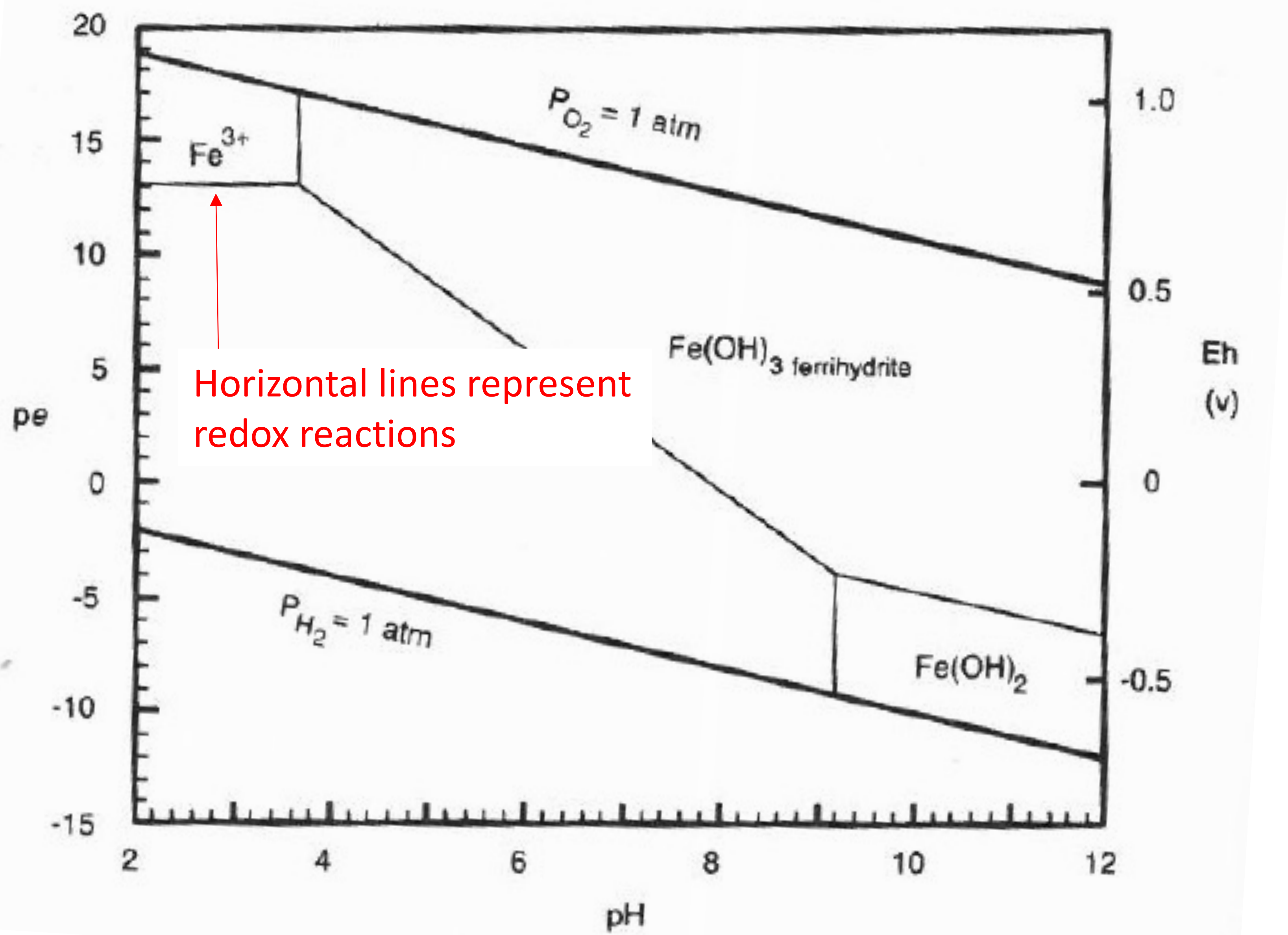

Fe-O-H_2O system at 25°C with ferrihydrite and $Fe(OH)_2$ as the iron oxide phases

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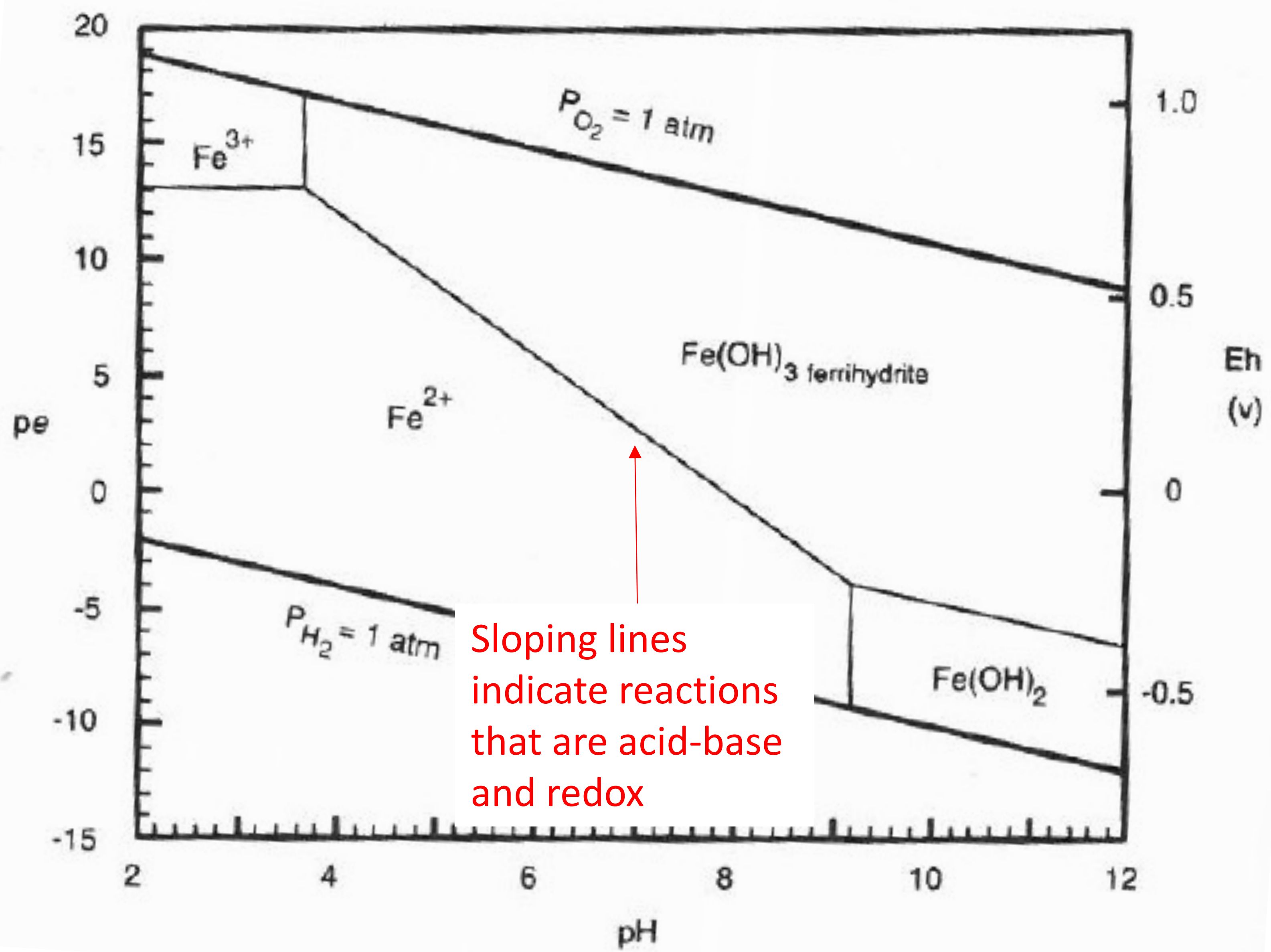
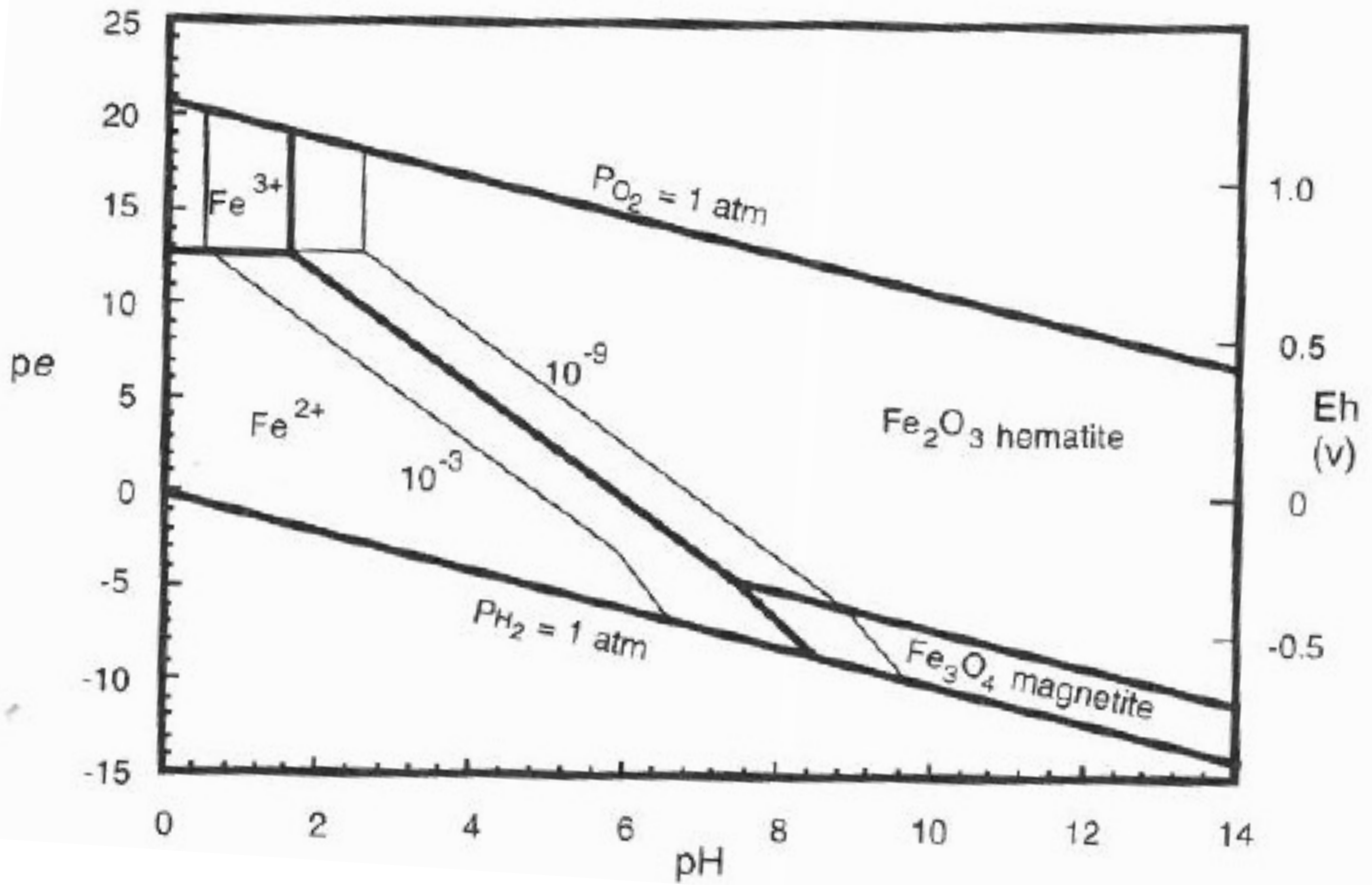


Fe-O-H_2O system at 25°C with ferrihydrite and $Fe(OH)_2$ as the iron oxide phases

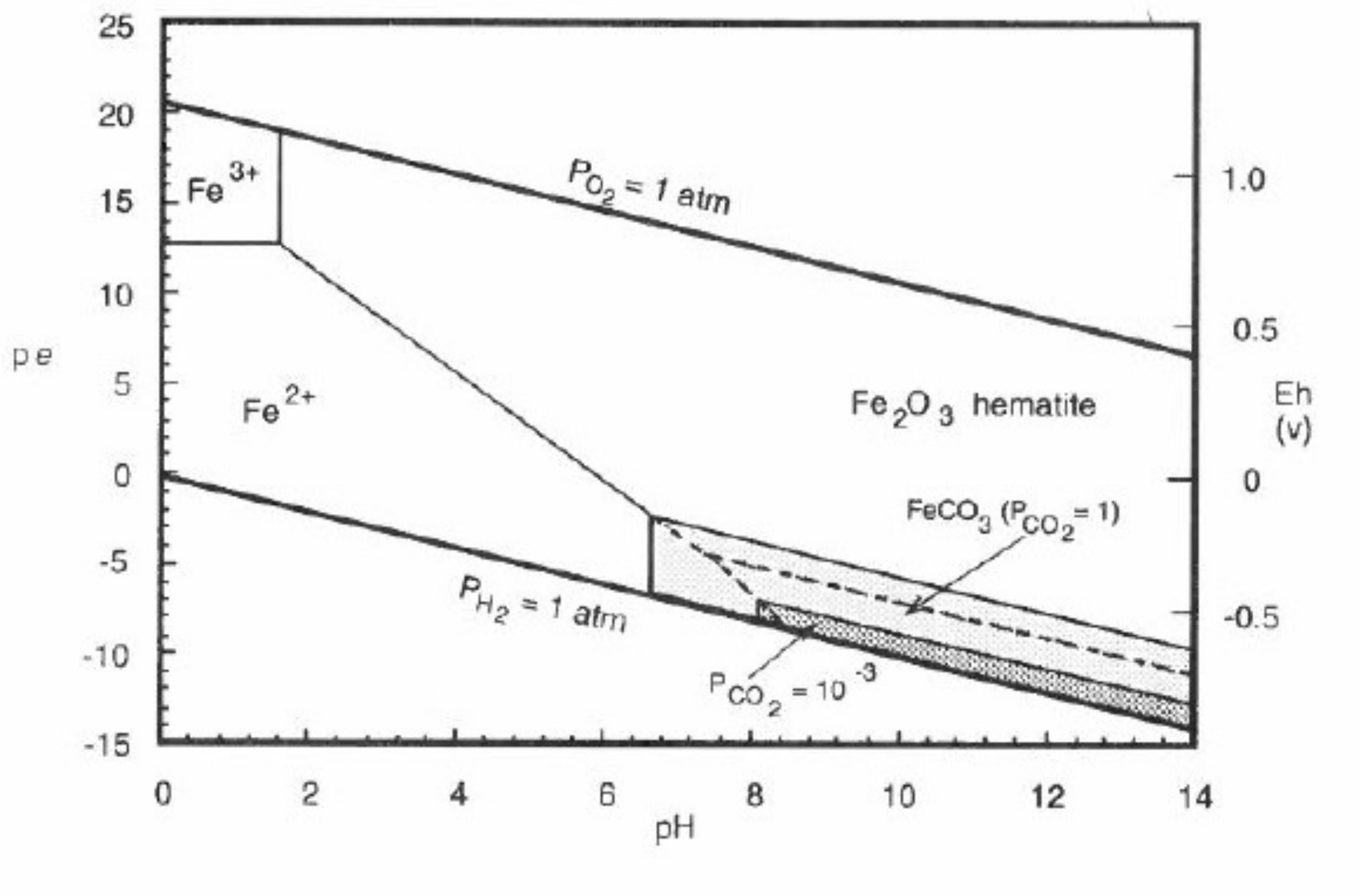
Geochemical species depend on the input parameters

Fe-O-H_2O system at 25°C with hematite and magnetite as the iron oxide phases

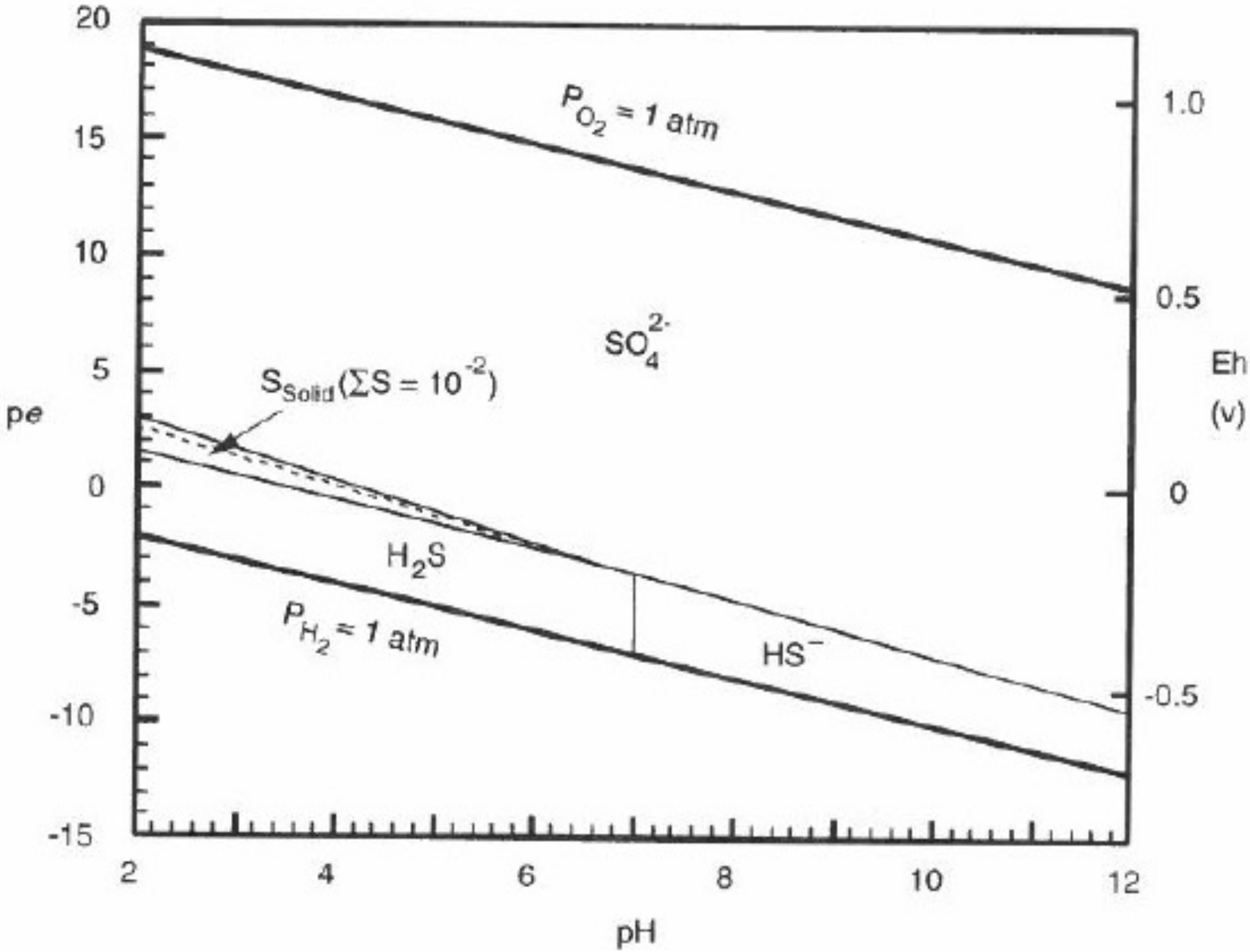


Geochemical species depend on the input parameters

Fe-O-H_2O-**CO_2** system at 25°C with hematite and magnetite as the iron oxide phases



Stability diagram for dissolved sulfur species



Eh-pH Stability Diagrams:

- Any point on the diagram will indicate the most thermodynamically stable (and theoretically most abundant) chemical species under given Eh and pH conditions for a given temperature and activity

- The stability fields displayed in the graph are calculated from thermodynamic equations and depend on **which species are considered** and their **activities** (or fugacities)