

## Oxidation-Reduction Equilibria

Advanced Aqueous Geochemistry  
DM Sherman, University of Bristol

### Oxidation States of Atoms and Ions

- The oxidation state of an atom in an elemental form is 0.

In  $O_2$ , O is in the 0 oxidation state.

- When bonded to something else, oxygen is in oxidation state -2 and hydrogen is in oxidation state of +1 (except for peroxide and superoxide).

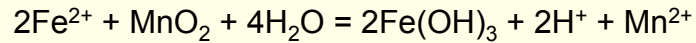
In  $CO_3^{2-}$ , O is in -2 state, C is in +4 state.

- The oxidation state of a single-atom ion is the charge on the ion.

For  $Fe^{2+}$ , Fe is in +2 oxidation state.

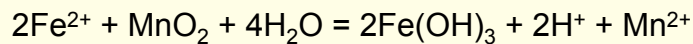
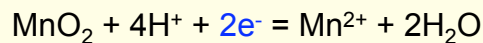
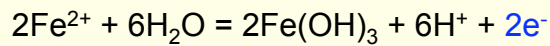
## Oxidation-Reduction Reactions

Consider the reaction



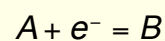
- $\text{Fe}^{2+}$  is being **oxidized** to  $\text{Fe}^{3+}$  (as  $\text{Fe}(\text{OH})_3$ )
- $\text{Mn}^{4+}$  (as  $\text{MnO}_2$ ) is being **reduced** to  $\text{Mn}^{2+}$

We can express the overall reaction as two half-reactions:



## K for half-reactions

For each half-reaction,



We can define an equilibrium constant

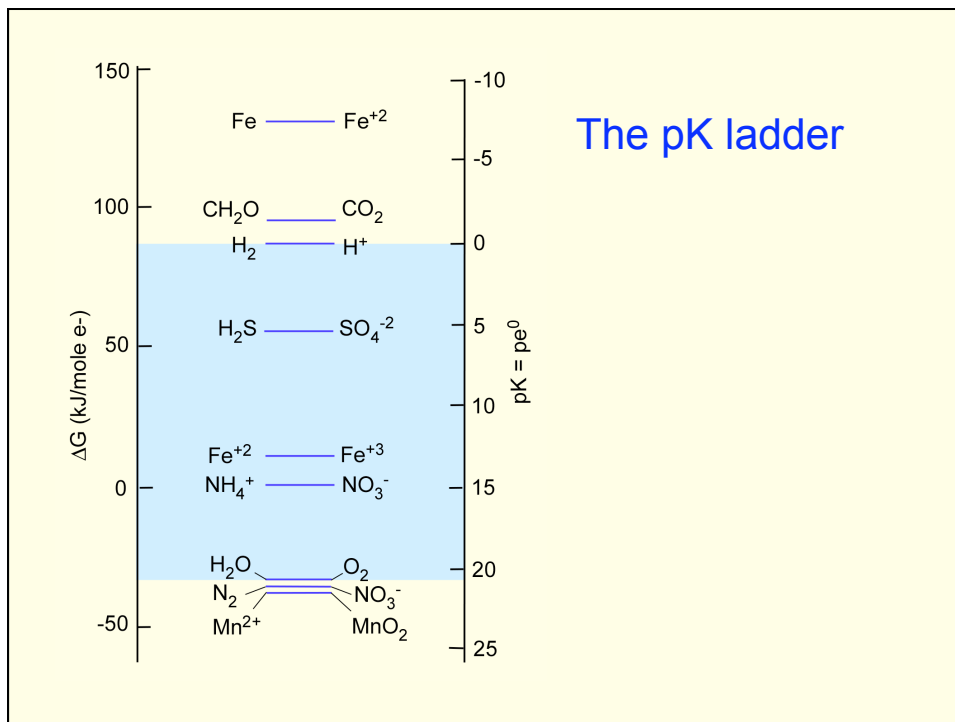
$$K = \frac{[B]}{[A][e^-]}$$

Where  $[e^-]$  is the activity of electrons. (*This does not mean that bare electrons are floating around in solution!!*) For convenience, take -log of the K expression to get

$$pK = pB - pA - pe$$

### Important half reactions

Reaction	pK
$1/4\text{O}_2 + \text{e}^- + \text{H}^+ = 1/2\text{H}_2\text{O}$	20.75
$2\text{H}^+ + \text{e}^- = \text{H}_2$	0
$\text{Cu}^{+2} + \text{e}^- = \text{Cu}^+$	-2.7
$\text{Fe}^{3+} + \text{e}^- = \text{Fe}^{2+}$	-13.02
$\text{MnO}_2 + 4 \text{H}^+ + 2 \text{e}^- = \text{Mn}^{+2} + 2 \text{H}_2\text{O}$	-41.38
$\text{CO}_3^{-2} + 10 \text{H}^+ + 8 \text{e}^- = \text{CH}_4 + 3 \text{H}_2\text{O}$	-41.07
$\text{SO}_4^{-2} + 9 \text{H}^+ + 8 \text{e}^- = \text{HS}^- + 4 \text{H}_2\text{O}$	-33.65
$2 \text{NO}_3^- + 12 \text{H}^+ + 10 \text{e}^- = \text{N}_2 + 6 \text{H}_2\text{O}$	-207.08



## The pe concept..

By analogy with pH, the pe ( $-\log[e^-]$ ) can be used to characterize the redox state of a system.

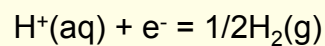
We can define an equilibrium constant

$$K = \frac{[B]}{[A][e^-]}$$

Where  $[e^-]$  is the activity of electrons. (*This does not mean that bare electrons are floating around in solution!!*)

## Range of pe of Aqueous Solutions

By convention,  $\Delta G^0 = 0.0$  for the reaction



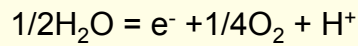
$$K = \frac{(p_{H_2})^{1/2}}{[H^+][e^-]} = 1$$

The *most reducing* condition that is possible at the Earth's surface will have  $p_{H_2} = 1$  bar. Hence,  $pH + pe = 0$  or

$$pH = -pe$$

## Range of pe of Aqueous Solutions (cont.)

The most oxidizing condition under which an aqueous solution can exist is buffered by the half-reaction

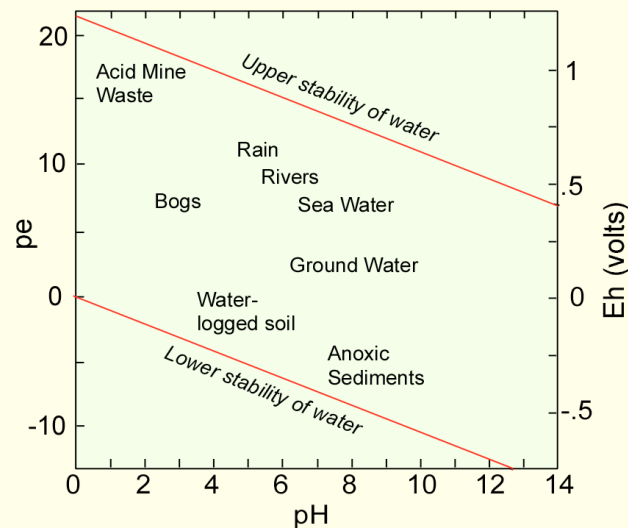


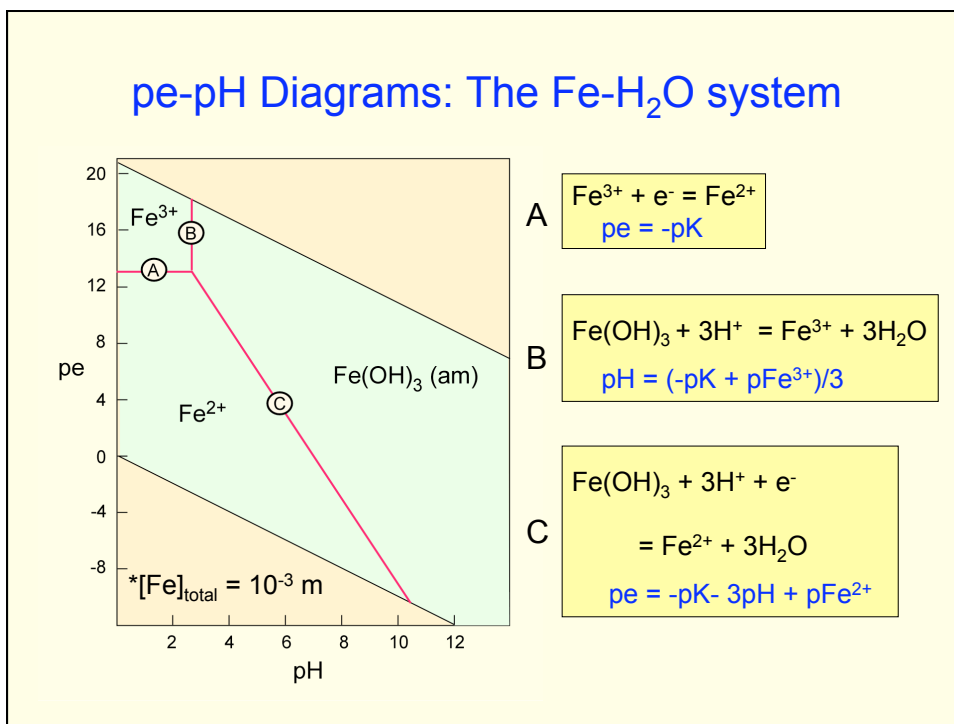
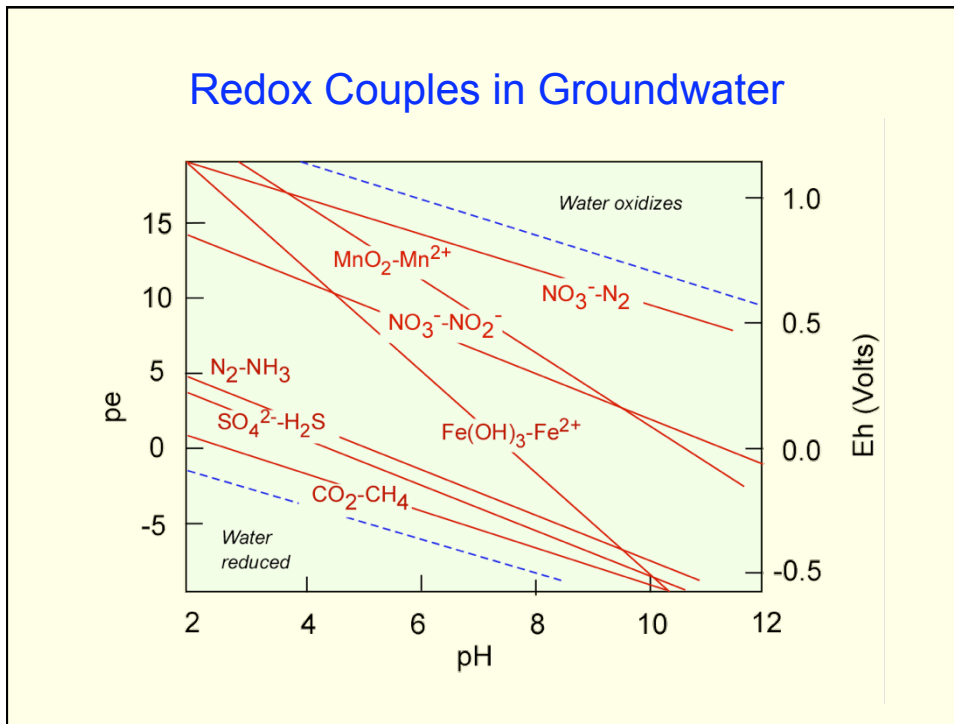
$$K = \frac{(p_{\text{O}_2})^{1/4} [\text{H}^+][e^-]}{[\text{H}_2\text{O}]^{1/2}} = 10^{-20.75}$$

Under the most oxidizing condition,  $p\text{O}_2 = 1$ . Since  $[\text{H}_2\text{O}] = 1$ , we have  $\text{pH} + \text{pe} = 20.75$  or

$$\text{pe} = 20.75 - \text{pH}$$

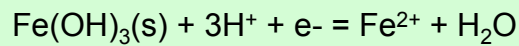
## pe-pH Environments





## Calculating pe from Concentrations

**Example:** Given that  $pK = -16.5$  for the half-reaction



calculate the pe of groundwater in which  $[\text{Fe}^{2+}] = 10^{-4} \text{ M}$ ,  $\text{pH} = 7$  and the solution is saturated in  $\text{Fe(OH)}_3$ .

*Solution:*

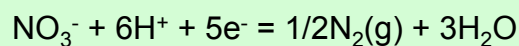
$$K = \frac{[\text{Fe}^{2+}]}{[\text{H}^+]^3[\text{e}^-]}$$

$$pK = p[\text{Fe}] - 3\text{pH} - pe$$

$$-16.5 = 4 - 21 - pe \quad \text{Hence, } pe = -0.5.$$

## Predicting Stability of Species

Would  $(\text{NO}_3)^-$  be stable in this groundwater?  $pK = -104.6$  for the reaction



$$K = \frac{(P_{\text{N}_2(\text{g})})^{1/2}}{[\text{NO}_3^-][\text{H}^+]^6[\text{e}^-]^5}$$

$$pK = -(1/2)\log(P_{\text{N}_2}) - p[\text{NO}_3^-] - 6\text{pH} - 5pe$$

Since,  $P_{\text{N}_2} = 0.8$ ,  $pe = -0.5$  and  $\text{pH} = 7$ , we get

$$-104.6 = -(1/2)(-0.097) - p[\text{NO}_3^-] - 42.0 + 2.5$$

$$p[\text{NO}_3^-] = 65.1$$

## Voltage and Free Energy

Charge x Voltage = Energy

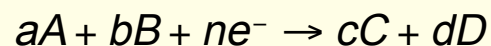
The free energy change ( $\Delta G$ ) associated with the transfer of  $n$  electrons is equivalent to a voltage drop ( $E$ ) experienced by the electrons:

$$\Delta G = -nFE$$

Where  $F$  is the faraday constant which is the charge (in coulombs) of a mole of electrons ( $F = 9.64846 \times 10^4$  C/mol).

## The Nernst Equation

By convention, we write half-reactions as reductions:



The voltage of this reaction is:

$$E = E^0 + \frac{RT}{nF} \ln \frac{[A]^a [B]^b}{[C]^c [D]^d}$$



## The Nernst Equation (cont.)

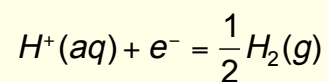
At 25 °C, we can write

$$E = E^0 + \frac{0.059}{n} \log \frac{[A]^a [B]^b}{[C]^c [D]^d}$$

Be careful with the sign convention. Notice the oxidized species are on top..

## The Standard Hydrogen Electrode

We assign a voltage of 0 for the reaction

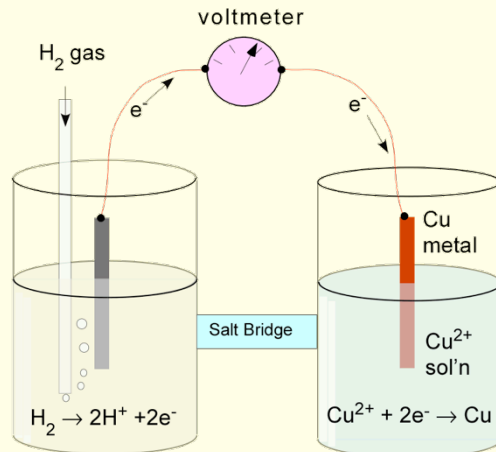


when  $[H^+] = 1$  mole/liter and  $P_{H_2}(g) = 1$  bar.

Hence,  $E^0$  for the  $H^+$  reduction is 0.

$$Eh = -0.059 \log(P_{H_2})^{1/2} - 0.059 pH$$

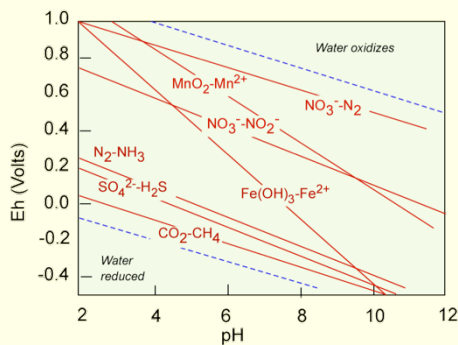
## The Standard Hydrogen Electrode



This cell would allow us to measure the E for the Cu<sup>2+</sup>-Cu half reaction relative to the S.H.E.

The salt bridge allows ions, but not electrons, to pass.

## What defines the Eh of a System?



Ideally, in a system where several of these redox couples are present, they would all be at equilibrium and give the same Eh value.

In practice, that is seldom the case. The Eh measured with a Pt electrode is determined by the most labile couple in the system.

## Dissolved Oxygen

- It is often difficult to get a reliable measurement of Eh (or pe). An alternative is to measure **dissolved oxygen**.

The solubility of oxygen in water is given by **Henry's law**:

$$[O_2] = K_H P_{O_2}$$

With  $K_H = 1.26 \times 10^{-3}$  M/L-bar at 25 °C

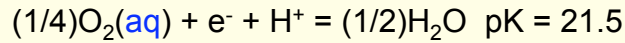
- Partial pressure of oxygen ( $O_2$ ) in atmosphere is 0.21 bar.
- Air-saturated water has a dissolved oxygen content of  $2.6 \times 10^{-4}$  mol  $O_2$ /liter or 8.5 mg/L.

## Berner's Classification of Sediments

<b>Oxic</b> $O_2 > 30\text{mM}$		$Fe_2O_3$ , FeOOH, $MnO_2$ No organic matter.
<b>Suboxic</b> $30\text{mM} > O_2 > 1\text{mM}$		$Fe_2O_3$ , FeOOH, $MnO_2$ Minor organic matter.
<b>Anoxic</b> $O_2 < 1\text{mM}$	<b>Sulfidic</b> $H_2S > 1\text{mM}$	$FeS_2$ , $MnCO_3$ , organic matter
	<b>Nonsulfidic</b> $H_2S < 1\text{mM}$	$FeCO_3$ , $Fe_3(PO_4)_2$ , $MnCO_3$ , low T Fe(II,III) silicates

## Dissolved Oxygen and pe

The pe corresponding to a dissolved oxygen concentration would be controlled by the reaction



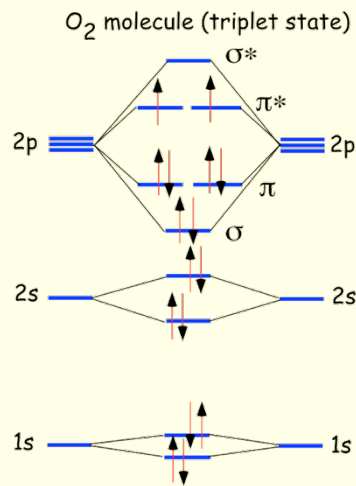
$$pe = 21.5 - pH + (1/4)\log[O_2(aq)]$$

In practice, the pe measured from Eh or derived from other redox couples will differ greatly from that derived from the dissolved O<sub>2</sub>.

## Redox Couples in Phreeqc

SOLUTION 1 SEAWATER FROM NORDSTROM ET AL. (1979)					
units	ppm				
pH	8.22				
pe	8.451	←	Default pe		
density	1.023				
temp	25.0				
redox	O(0)/O(-2)	←	Couple which determines pe		
Fe	0.002	←	Speciate using pe from O(0)		
Zn	0.001				
Mn	0.0002	pe	←	Use default pe	
Al	0.0008				
Si	4.28				
Cl	19353.0	charge			
S(6)	2712.0			←	Use input values; do not speciate
N(5)	0.29	gfw	62.0	←	Use input values; do not speciate
N(-3)	0.03	as	NH4	←	
O(0)	1.0	O2(g)	-0.7	←	Equilibrate with atmosphere
Alkalinity	141.682	as	HCO3	←	

## Kinetics of Oxidation by O<sub>2</sub>



- The oxidation of organic molecules by triplet oxygen is spin-forbidden. Hence oxidation by triplet O<sub>2</sub> is very slow.

## Peroxide, Superoxide and Ozone..

- Peroxide and superoxide are reactive intermediates resulting from the oxidation of species by oxygen.
- Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) has O in an oxidation state = -1.
- Superoxide (O<sub>2</sub><sup>-1</sup>) has O in an oxidation state = -1/2.
- The mineral pyrite (FeS<sub>2</sub>) is a persulfide.
- Ozone (O<sub>3</sub>) has oxygen in an oxidation state of +2/3.

## Summary

- Understand oxidation-reduction reactions and oxidation states.
- Nernst Equation.
- Eh-pH diagrams.
- Redox environments in nature.
- Calculate Eh from concentrations.
- Prediction of stable oxidation states.