

Redox potential, pH-pE

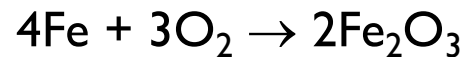
- Redox potential – potential for an electrical cell to do work
- Relationship between Gibbs Free Energy and Redox Potential
- Describing environmental systems redox potential
- pH-pE (Pourbaix) diagrams

Redox Potential: The Fundamentals

- **Redox potential** expresses the tendency of an environment to receive or supply electrons (ability to do electrical work)

- An **oxic** environment has high redox potential because **O₂** is available as an **electron acceptor**

For example, Fe oxidizes to rust in the presence of O₂ because the iron shares its electrons with the O₂:



- In contrast, an **anoxic** environment has low redox potential because of the **absence of O₂**

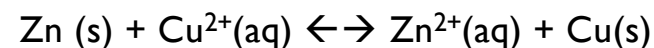
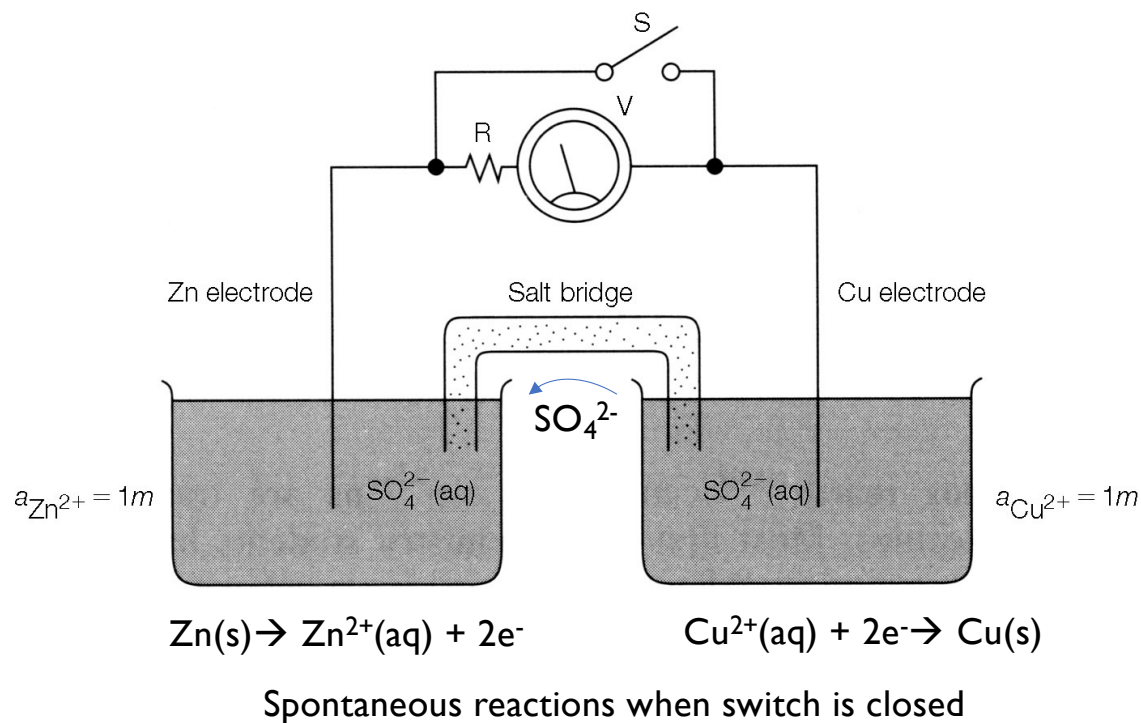
the more positive the potential, the greater the species' affinity for electrons and tendency to be reduced

Table 18.1 Relative Strengths of Oxidizing and Reducing Agents

	Oxidizing Agent		Reducing Agent	
↑	$F_2(g) + 2e^-$	→	$2 F^-$	↑
	$Cl_2(g) + 2e^-$	→	$2 Cl^-$	
	$\frac{1}{2} O_2(g) + 2 H^+ + 2e^-$	→	H_2O	
	$Br_2(l) + 2e^-$	→	$2 Br^-$	
	$NO_3^- + 4 H^+ + 3e^-$	→	$NO(g) + 2 H_2O$	
	$Ag^+ + e^-$	→	$Ag(s)$	
	$Fe^{3+} + e^-$	→	Fe^{2+}	
	$I_2(s) + 2e^-$	→	$2 I^-$	
	<u>$Cu^{2+} + 2e^-$</u>	→	<u>$Cu(s)$</u>	
	$2 H^+ + 2e^-$	→	$H_2(g)$	
	$Ni^{2+} + 2e^-$	→	$Ni(s)$	
	$Co^{2+} + 2e^-$	→	$Co(s)$	
	$Cd^{2+} + 2e^-$	→	$Cd(s)$	
	$Fe^{2+} + 2e^-$	→	$Fe(s)$	
	<u>$Zn^{2+} + 2e^-$</u>	→	<u>$Zn(s)$</u>	
	$Al^{3+} + 3e^-$	→	$Al(s)$	
	$Na^+ + e^-$	→	$Na(s)$	
	$Ca^{2+} + 2e^-$	→	$Ca(s)$	
	$Li^+ + e^-$	→	$Li(s)$	
↓				↓

Note: Strengths not necessarily related to
of electrons transferred

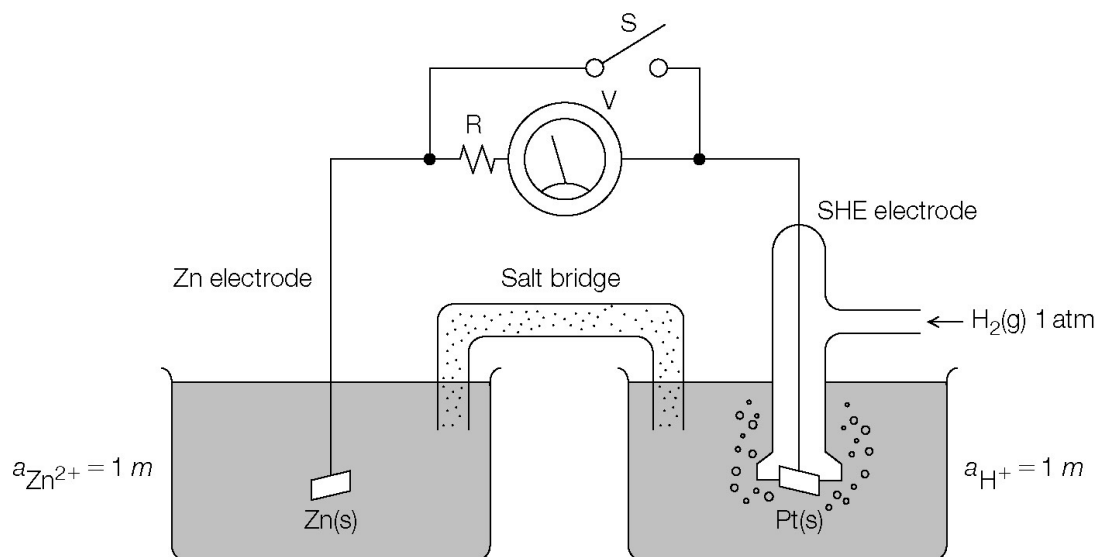
A Simple Electrochemical Cell



- Start at non-equilibrium concentrations
- Charge remains neutral (sulfate ions flow to balance)
- Voltmeter measures electron flow
 - With switch open, voltage difference measures electrical work that can be done by this cell
 - The **voltage** is characteristic for any set of chemical conditions
- Cu is a stronger oxidizing agent (takes on electrons) than Zn, which dictates the direction of electron and ion flow here

Standard Hydrogen Electrode

- Determining the relative affinities of a redox couple for electrons lets us predict reaction directions / whether a reaction will occur
 - Need a standard of comparison: Standard Hydrogen Electrode



Reaction occurring in the SHE (right hand side):
 $2H^+ + 2e^- \leftrightarrow H_2(g)$

By convention, the **standard electrode potential (E_h^0)** of SHE = 0V

If E_h^0 of a reduction half reaction is >0 , that couple can oxidize the SHE.

If E_h^0 is negative, will reduce the SHE (H can gain or lose electrons)

Common half reactions relative to SHE

Table 3.7. Common redox half-reactions and corresponding E_h^0 , $E_{h,water}^0$, pe^0 and pe_{water}^0 ^a values

Half-reaction	E_h^0	$E_{h,water}^0$ ^a	pe^0	pe_{water}^0
$\frac{1}{4}O_2(g) + H^+ + e^- \rightarrow \frac{1}{2}H_2O$	+1.23	+0.81	+20.75	+13.75
$\frac{1}{5}NO_3^- + \frac{6}{5}H^+ + e^- \rightarrow \frac{1}{10}N_2(g) + \frac{3}{5}H_2O$	+1.25	+0.75	+21.05	+12.65
$\frac{1}{2}MnO_2 + 2H^+ + e^- \rightarrow \frac{1}{2}Mn^{2+} + H_2O$	+1.29	+0.46	+21.80	+7.80
$\frac{1}{2}NO_3^- + H^+ + e^- \rightarrow \frac{1}{2}NO_2^- + \frac{1}{2}H_2O$	+0.84	+0.42	+14.15	+7.15
$\frac{1}{8}NO_3^- + \frac{5}{4}H^+ + e^- \rightarrow \frac{1}{8}NH_4^+ + \frac{3}{8}H_2O$	+0.88	+0.36	+14.90	+6.15
$FeOOH(s) + 3H^+ + e^- \rightarrow Fe^{2+} + 2H_2O$	+0.94	-0.30	+16.0	-5.0
$\frac{1}{2}CH_2O + H^+ + e^- \rightarrow \frac{1}{2}CH_3OH$	+0.24	-0.18	+3.99	-3.01
$\frac{1}{8}SO_4^{2-} + \frac{9}{8}H^+ + e^- \rightarrow \frac{1}{8}HS^- + \frac{1}{2}H_2O$	+0.25	-0.22	+4.25	-3.75
$\frac{1}{8}CO_2(g) + H^+ + e^- \rightarrow \frac{1}{8}CH_4(g) + \frac{1}{4}H_2O$	+0.17	-0.24	+2.87	-4.13
$\frac{1}{6}N_2(g) + \frac{4}{3}H^+ + e^- \rightarrow \frac{1}{3}NH_4^+$	+0.28	-0.28	+4.68	-4.68
$H^+ + e^- \rightarrow \frac{1}{2}H_2(g)$	0.00	-0.41	0.00	-7.00
$\frac{1}{4}CO_2(g) + H^+ + e^- \rightarrow \frac{1}{4}CH_2O + \frac{1}{4}H_2O$	-0.071	-0.48	-1.20	-8.20

^a Values are calculated for unit activities of oxidant and reactant in neutral water of pH = 7.0 at 25 °C and 1 atm. Half-reactions are listed in order of decreasing pe_{water}^0 , and hence of decreasing oxidizing power at pH 7. E_h values are in volts.

Relating standard electrode potential (E_h^0) to Gibbs free energy (ΔG_r^0)

An electrochemical cell is capable of doing work – by driving electrons across a potential difference.

This can be measured as a change in free energy:

$$\Delta G_r^0 = -nFE_h^0$$

where

n = number of moles of electrons (*equivalents*) involved in the reaction

F = *Faraday constant* = 23.1 kcal V⁻¹ equiv⁻¹

E_h^0 = the *standard electrode / cell potential* (V) at standard state

Nernst Equation:

How we relate reduction potential of a reaction to its standard electrode potential, given a specific T and activities

We know from a previous class:

$$\Delta G = \Delta G^\circ + RT \ln \frac{\{\text{products}\}^x}{\{\text{reactants}\}^y}$$

← reduced species
← oxidized species

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Substituting $\Delta G = -nFE$, we get the **Nernst Equation**:

$$E = E^\circ - \frac{RT}{nF} \ln \frac{\{\text{products}\}^x}{\{\text{reactants}\}^y}$$

Or:

$$E = E^\circ + \frac{RT}{nF} \ln \frac{\{\text{reactants}\}^y}{\{\text{products}\}^x}$$

*at 25C,
R=8.314 J mol⁻¹ deg⁻¹
RT/F = 0.0592

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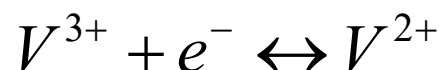
At 298°K:

$$E = E^\circ + \frac{0.0592}{n} \log \frac{\{\text{reactants}\}^y}{\{\text{products}\}^x}$$

Important points:

- Geochemists usually use the symbol E_h instead of E (indicating the hydrogen scale is being used)
- The Nernst Equation relates the E_h of a cell to the standard E_h and to the activities of reactants and products under given conditions
- When at standard state (all activities = 1), $E_h = E^\circ$
- We can use E_h as an indicator of the state of natural waters:

Example #1: Use Eh values to Calculate Vanadium Speciation

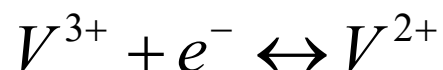


What species of V dominates in seawater?

$$Eh = Eh^{\circ} + \frac{0.059}{1} \log \left\{ \frac{V^{3+}}{V^{2+}} \right\}$$

1. Assume measured Eh = 0.729 V

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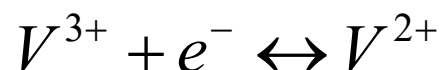
1. Assume measured Eh = 0.729 V

8.3 Electrode Potential: Nernst Equation and the Electrochemical Cell 445

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	pe°
$Na^{+} + e^{-} = Na(s)$	-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	-7.45
$Co^{2+} + 2e^{-} = Co(s)$	-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

Example #1: Use Eh values to Calculate Vanadium Speciation



What species of V dominates in seawater?

$$Eh = Eh^{\circ} + \frac{0.059}{1} \log \left\{ \frac{V^{3+}}{V^{2+}} \right\}$$

1. Assume measured $E_H = 0.729$ V

2. From Stumm and Morgan

Table 8.3: $E_H^{\circ} = -0.26$

1. Plug into equation:

$\therefore V^{3+}$ dominates

$$\begin{aligned} 0.729 &= -0.26 + 0.059 \log \left\{ \frac{V^{3+}}{V^{2+}} \right\} \\ 0.989 &= 0.059 \log \left\{ \frac{V^{3+}}{V^{2+}} \right\} \\ 16.8 &= \log \left\{ \frac{V^{3+}}{V^{2+}} \right\} \\ \left\{ \frac{V^{3+}}{V^{2+}} \right\} &= 6 \times 10^{16} \end{aligned}$$

Redox Potential in Nature

- A mixture of constituents, not really separate cells
- We insert an inert **Pt electrode** into an environment and measure the voltage relative to a standard electrode
[Std. electrode = H₂ gas above solution of known pH (theoretical, not practical). More practical electrodes are calibrated using this H₂ electrode.]

- Example: when O₂ is present, electrons migrate to the Pt electrode:



- The electrons are generated from H₂ gas:

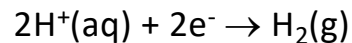


- **Voltage** between electrodes measures the **redox potential**

Definition of pE – activity of electrons

$$E = E^\circ - \frac{RT}{nF} \ln \frac{\{products\}^x}{\{reactants\}^y}$$

Take the reaction in the Standard Hydrogen Electrode



$$E_H = E_H^\circ - \frac{RT}{nF} \times \ln \left(\frac{(\text{H}_2)^{\frac{1}{2}}}{(\text{H}^+)(\text{e}^-)} \right)$$

In the standard state, activities of H_2 and H^+ are 1 and at equilibrium $E_H = 0$, so:

$$\frac{E_H^\circ F}{2.3RT} = -\log_{10}(\text{e}^-) = pe^0 \quad \text{Standard } pe;$$

$$* \ln(I/\text{e}^-) = 2.3 \times -\log_{10}(\text{e}^-)$$

$$pe = pe^0 - \frac{1}{n} \log_{10} \frac{(D)^d (E)^e}{(B)^b (C)^c}$$

Analogous to how pH defines activity of H^+ : $\text{pH} = -\log_{10}(\text{H}^+)$

Plots of pE-pH describe stability conditions

Example #2: Calculation of pE

Assume:

- pE in a given environment is controlled by this reaction:



$$(\because n = 1)$$

- $\{\text{Fe}^{3+}\} = 10^{-5}$
- $\{\text{Fe}^{2+}\} = 10^{-3}$

Electrochemical Cells - 3

TABLE 7.1
Standard Electrode Potentials for Selected Half-Reactions

Reaction	Log K at 25°C	Standard Electrode Potential (V) at 25°C
$\text{Na}^+ + e^- = \text{Na(s)}$	-46	-2.71
$\text{Zn}^{2+} + 2e^- = \text{Zn(s)}$	-26	-0.76
$\text{Fe}^{2+} + 2e^- = \text{Fe(s)}$	-14.9	-0.44
$\text{Co}^{2+} + 2e^- = \text{Co(s)}$	-9.5	-0.28
$\text{V}^{3+} + e^- = \text{V}^{2+}$	-4.3	-0.26
$2\text{H}^+ + 2e^- = \text{H}_2(\text{g})$	0.0	0.00
$\text{S(s)} + 2\text{H}^+ + 2e^- = \text{H}_2\text{S}$	+4.8	+0.14
$\text{Cu}^{2+} + e^- = \text{Cu}^+$	+2.7	+0.16
$\text{AgCl(s)} + e^- = \text{Ag(s)} + \text{Cl}^-$	+3.7	+0.22
$\text{Cu}^{2+} + 2e^- = \text{Cu(s)}$	+11.4	+0.34
$\text{Cu}^+ + e^- = \text{Cu(s)}$	+8.8	+0.52
$\text{Fe}^{3+} + e^- = \text{Fe}^{2+}$	+13.0	+0.77
$\text{Ag}^+ + e^- = \text{Ag(s)}$	+13.5	+0.80
$\text{Fe(OH)}_3(\text{s}) + 3\text{H}^+ + e^- = \text{Fe}^{2+} + 3\text{H}_2\text{O}$	+17.1	+1.01
$\text{IO}_3^- + 6\text{H}^+ + 5e^- = \frac{1}{2}\text{I}_2(\text{s}) + 3\text{H}_2\text{O}$	+104	+1.23
$\text{MnO}_2(\text{s}) + 4\text{H}^+ + 2e^- = \text{Mn}^{2+} + 2\text{H}_2\text{O}$	+43.6	+1.29
$\text{Cl}_2(\text{g}) + 2e^- = 2\text{Cl}^-$	+46	+1.36
$\text{Co}^{3+} + e^- = \text{Co}^{2+}$	+31	+1.82

Source: From *Aquatic Chemistry*, W. Stumm and J. J. Morgan, copyright © 1981 by John Wiley & Sons, Inc., New York, p. 437. Reprinted by permission.

Example #2: Calculation of pE

Assume:

- pE in a given environment is controlled by this reaction:



($\therefore n = 1$)

- $\{\text{Fe}^{3+}\} = 10^{-5}$
- $\{\text{Fe}^{2+}\} = 10^{-3}$

$$pE = pE^\circ + \frac{1}{n} \log \left\{ \frac{\text{oxid}}{\text{reduc}} \right\}$$

$$pE^\circ = \frac{\log(K)}{n} = 13.0$$

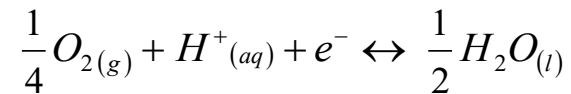
$$\therefore pE = 13.0 + \log \left(\frac{10^{-5}}{10^{-3}} \right) = 11.0$$

$$\{e^-\} = 10^{-11}$$

Example #3: Effect of Atmospheric O₂

Assume: Natural water at pH 7.5 in equilibrium with the atmosphere

$$P_{O_2} = 0.21 atm \quad \therefore \{O_2\} = 0.21$$

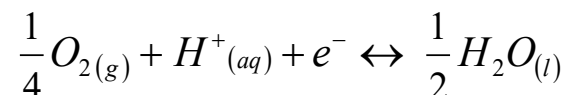


$$pE^\circ = 20.75 \quad \text{Table 3.7 Emerson and Hedges}$$

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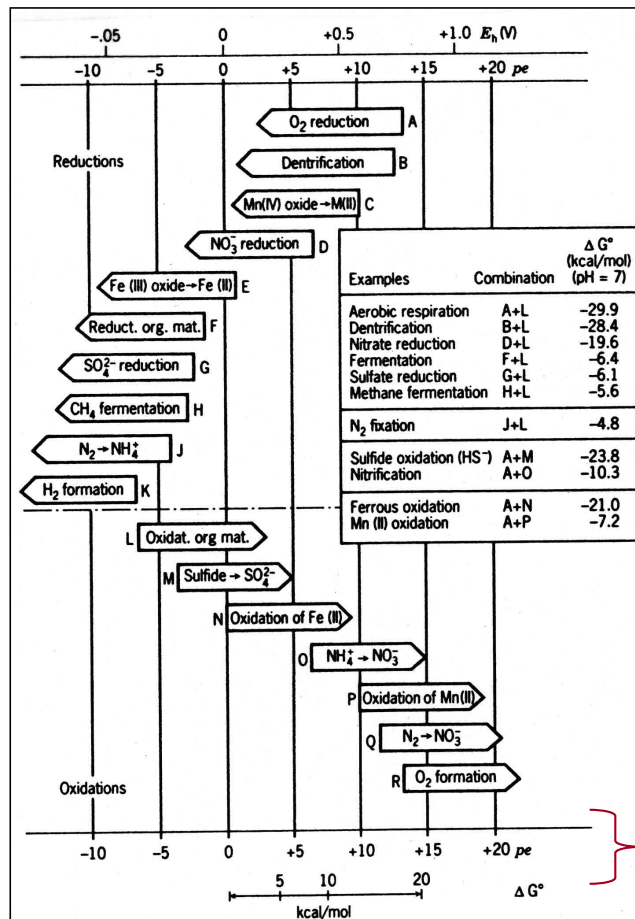
$$pE^\circ = 20.75 \quad \text{Table 3.7 Emerson and Hedges}$$

$$pE = pE^\circ + \frac{1}{n} \log \frac{\{O_2\}^{\frac{1}{4}} \{H^+\}}{\{H_2O\}^{\frac{1}{2}} \rightarrow 1} \quad \{H^+\} = 10^{-7.5}$$

$$pE = 13.08 \quad \therefore \{e^-\} = 10^{-13.08}$$

Conclusion: This environment has lower electron activity than Example #2, and is thus more oxidizing

Redox Reactions Have Characteristic pE Values



$$pE = \frac{F}{2.3RT} E_H$$

$$pE = \frac{-\Delta G}{2.3nRT}$$

FIGURE 7.4. Sequence of microbially mediated redox reactions. The arrows point in the direction of the spontaneous redox reaction. The originating point of the arrows indicates the redox energy associated with each half-reaction. No information is contained in the relative length of the arrows.

pE-pH Diagrams - I

pE-pH stability field diagrams show in a comprehensive way how protons (pH) and electrons (pE) simultaneously shift equilibria of reactions under various conditions.

These diagrams also indicate which species predominate under any given condition of pE and pH.

Two equations are used to produce the diagrams:

$$pE = pE^{\circ} + \frac{1}{n} \log \frac{\{oxid\}^o}{\{reduc\}^r}$$
$$pE^{\circ} = \frac{1}{n} \log K$$

pE-pH Diagrams – Water stability

Oxidizing limit of diagrams: $\frac{1}{4} \text{O}_2 + \text{H}^+ + \text{e}^- \rightarrow \frac{1}{2} \text{H}_2\text{O}$

$$pE^\circ = +20.75$$

$$n = 1$$

$$\text{pH} = -\log\{\text{H}^+\}$$

$$\text{Set limit: } \{\text{O}_2\} = 1$$

$$pE = pE^\circ + \frac{1}{n} \log \frac{\{\text{O}_2\}^{1/4} \{\text{H}^+\}}{\{\text{H}_2\text{O}\}^{1/2}}$$

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

Reducing limit of diagrams: $\text{H}_2\text{O} + \text{e}^- \rightarrow \frac{1}{2} \text{H}_2 + \text{OH}^-$



$$pE^\circ = 0.0$$

$$n = 1$$

$$\text{pH} = -\log\{\text{H}^+\}$$

$$\text{Set limit: } \{\text{H}_2\} = 1$$

$$pE = pE^\circ + \frac{1}{n} \log \frac{\{\text{H}^+\}}{\{\text{H}_2\}^{1/2}}$$

$$pE = -\text{pH}$$

TABLE 7.3
Log K , pe^0 , and $E_h^0(w)$ of Redox Processes^a

Reaction	pe^0 ($\equiv \log K$)	pe_w^{0a}	$E_h^0(w)$
(1) $\frac{1}{4}O_2(g) + H^+ + e^- = \frac{1}{2}H_2O$	+20.75	+13.75	+0.81
(2) $\frac{1}{3}NO_3^- + \frac{5}{3}H^+ + e^- = \frac{1}{10}N_2(g) + \frac{3}{2}H_2O$	+21.05	+12.65	+0.75
(3) $\frac{1}{2}MnO_2(s) + \frac{1}{2}HCO_3^-(10^{-3}M) + \frac{3}{2}H^+ + e^- = \frac{1}{2}MnCO_3(s) + \frac{3}{8}H_2O$	—	+3.9 ^b	+0.23
(4) $\frac{1}{2}NO_3^- + H^+ + e^- = \frac{1}{2}NO_2^- + \frac{1}{2}H_2O$	+14.15	+7.15	+0.42
(5) $\frac{1}{8}NO_3^- + \frac{1}{4}H^+ + e^- = \frac{1}{8}NH_4^+ + \frac{3}{8}H_2O$	+14.90	+6.15	+0.36
(6) $\frac{1}{6}NO_2^- + \frac{1}{3}H^+ + e^- = \frac{1}{6}NH_4^+ + \frac{1}{3}H_2O$	+15.14	+5.82	+0.34
(7) $\frac{1}{2}CH_3OH + H^+ + e^- = \frac{1}{2}CH_4(g) + \frac{1}{2}H_2O$	+9.88	+2.88	+0.17
(8) $\frac{1}{4}CH_2O + H^+ + e^- = \frac{1}{4}CH_4(g) + \frac{1}{4}H_2O$	+6.94	-0.06	+0.00
(9) $FeOOH(s) + HCO_3^-(10^{-3}M) + 2H^+ + e^- = FeCO_3(s) + 2H_2O$	—	-0.8 ^b	-0.05
(10) $\frac{1}{2}CH_2O + H^+ + e^- = \frac{1}{2}CH_3OH$	+3.99	-3.01	-0.18
(11) $\frac{1}{6}SO_4^{2-} + \frac{1}{3}H^+ + e^- = \frac{1}{6}S(s) + \frac{1}{3}H_2O$	+6.03	-3.30	-0.20
(12) $\frac{1}{8}SO_4^{2-} + \frac{1}{4}H^+ + e^- = \frac{1}{8}H_2S(g) + \frac{1}{2}H_2O$	+5.25	-3.50	-0.21
(13) $\frac{1}{8}SO_4^{2-} + \frac{9}{8}H^+ + e^- = \frac{1}{8}HS^- + \frac{1}{2}H_2O$	+4.25	-3.75	-0.22
(14) $\frac{1}{2}S(s) + H^+ + e^- = \frac{1}{2}H_2S(g)$	+2.89	-4.11	-0.24
(15) $\frac{1}{8}CO_2(g) + H^+ + e^- = \frac{1}{8}CH_4(g) + \frac{1}{4}H_2O$	+2.87	-4.13	-0.24
(16) $\frac{1}{6}N_2(g) + \frac{1}{3}H^+ + e^- = \frac{1}{3}NH_4^+$	+4.68	-4.68	-0.28
(17) $\frac{1}{2}(NADP^+) + \frac{1}{2}H^+ + e^- = \frac{1}{2}(NADPH)$	-2.0	-5.5	-0.33
(18) $H^+ + e^- = \frac{1}{2}H_2(g)$	0.0	-7.00	-0.41
(19) Oxidized ferredoxin + e^- = reduced ferredoxin	-7.1	-7.1	-0.42
(20) $\frac{1}{4}CO_2(g) + H^+ + e^- = \frac{1}{24}(\text{glucose}) + \frac{1}{4}H_2O$	-0.20	-7.20	-0.43
(21) $\frac{1}{2}HCOO^- + \frac{1}{2}H^+ + e^- = \frac{1}{2}CH_2O + \frac{1}{2}H_2O$	+2.82	-7.68	-0.45
(22) $\frac{1}{4}CO_2(g) + H^+ + e^- = \frac{1}{4}CH_2O + \frac{1}{4}H_2O$	-1.20	-8.20	-0.48
(23) $\frac{1}{2}CO_2(g) + \frac{1}{2}H^+ + e^- = \frac{1}{2}HCOO^-$	-4.83	-8.33	-0.49

Source: From *Aquatic Chemistry*, W. Stumm and J. J. Morgan, copyright © 1970 by John Wiley & Sons, Inc., New York, p. 318. Reprinted by permission. See Stumm and Morgan (1970) for data sources.

^aValues for pe_w^0 apply to the electron activity for unit activities of oxidant and reductant in neutral water, that is, at pH = 7.0 for 25°C.

^bThese data correspond to $(HCO_3^-) = 10^{-3} M$ rather than unity and so are not exactly pe_w^0 ; they represent typical aquatic conditions more nearly than pe_w^0 values do.

pE-pH Diagrams - water

Oxidizing limit of diagrams:

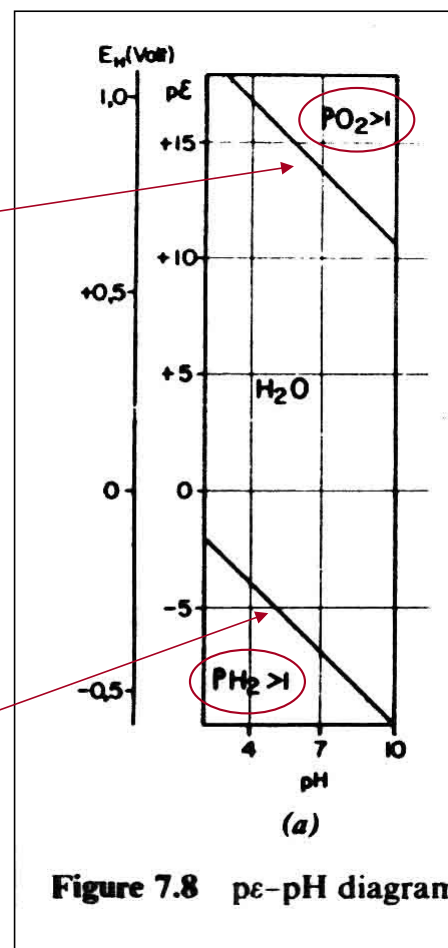


$$pE = 20.75 - pH$$

Reducing limit of diagrams:

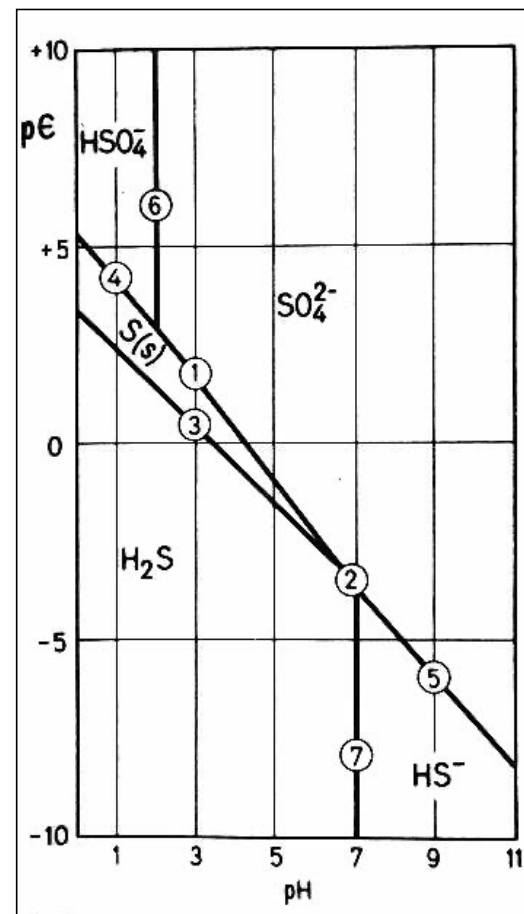


$$pE = -pH$$



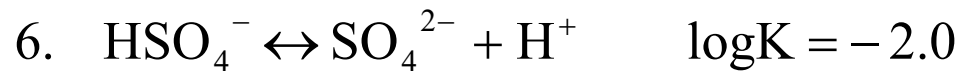
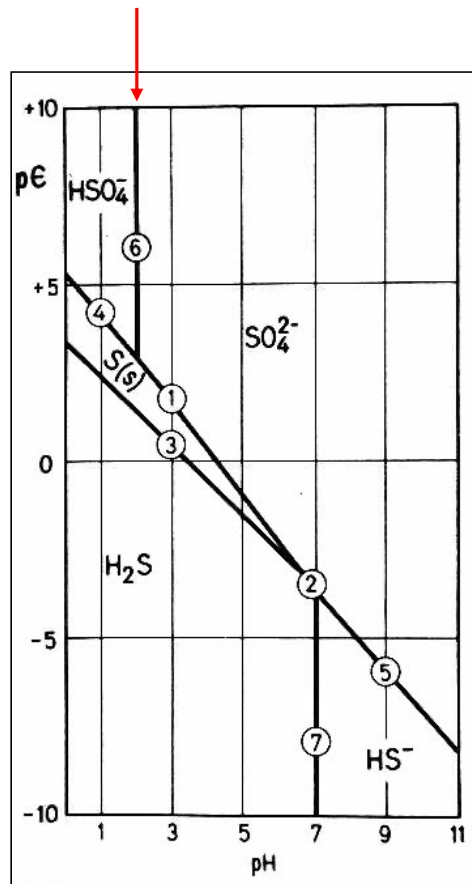
pE-pH Diagrams - 4

- *Phase-boundary lines* on a pE-pH diagram indicate *stability field* boundaries – defined as lines where *activities of both adjacent dominant species are equal*.
- Lines are defined by reactions between adjacent dominant species
- Reactions must have known *log K* or *pE°* values.



Construction of pE-pH Diagram - I

Acid-base reactions with no pE dependency



$$K = \frac{\{ \text{SO}_4^{2-} \} \{ \text{H}^+ \}}{\{ \text{HSO}_4^- \}}$$

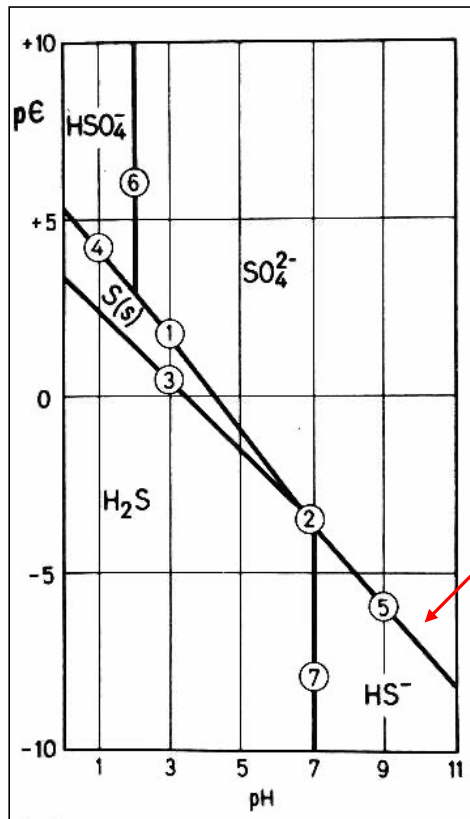
*pH = -log{H⁺}

$$\log K = -2.0 = \log \left\{ \frac{\text{SO}_4^{2-}}{\text{HSO}_4^-} \right\} - \text{pH}$$

When $\{ \text{SO}_4^{2-} \} = \{ \text{HSO}_4^- \}, \quad \text{pH} = 2.0$

Construction of pE-pH Diagram - 2

Redox reactions of dissolved species



$$pE = pE^\circ + \frac{1}{8} \log \frac{\{ \text{SO}_4^{2-} \} \{ \text{H}^+ \}^9}{\{ \text{HS}^- \} \{ \text{H}_2\text{O} \}^4} = 1$$

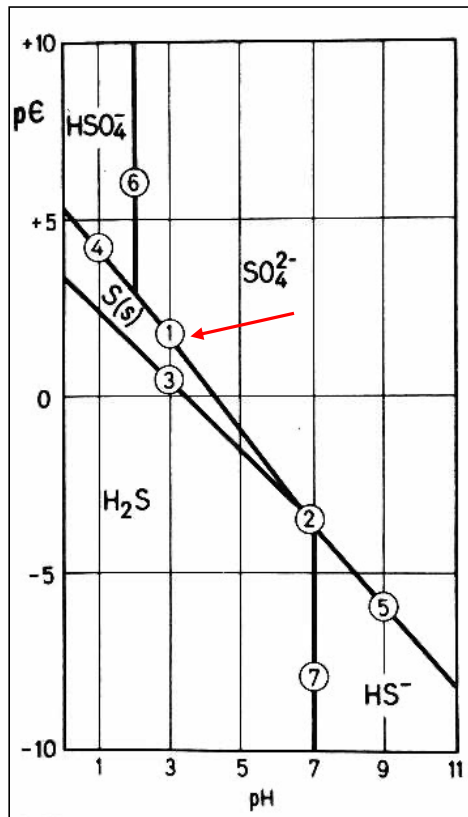
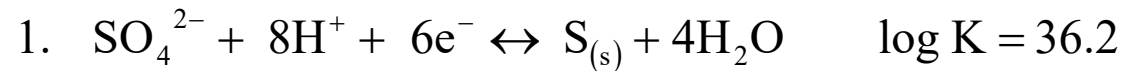
$$pE^\circ = \frac{1}{n} \log K = \frac{34}{8}$$

$$pE = \frac{34}{8} + \frac{1}{8} \log \frac{\{ \text{SO}_4^{2-} \}}{\{ \text{HS}^- \}} - \frac{9}{8} pH$$

$$\text{When } \{ \text{SO}_4^{2-} \} = \{ \text{HS}^- \}, \quad pE = \frac{34}{8} - \frac{9}{8} pH$$

Construction of pE-pH Diagram - 3

Redox reactions of dissolved and solid species



$$pE = \frac{36.2}{6} + \frac{1}{6} \log \frac{\{SO_4^{2-}\} \{H^+\}^8}{\{S_{(s)}\} \{H_2O\}^4} = 1$$

$$pE = \frac{36.2}{6} + \frac{1}{6} \log \{SO_4^{2-}\} - \frac{8}{6} pH$$

$$\text{When } \{SO_4^{2-}\} = 10^{-2}, \quad pE = 5.70 - \frac{8}{6} pH$$

Activity of dissolved species must be given

Marine Sediment Depth Profiles

Reaction	E_h (V)	ΔG
Reduction of O_2		
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	+0.812	-29.9
Reduction of NO_3^-		
$2NO_3^- + 6H^+ + 6e^- \rightarrow N_2 + 3H_2O$	+0.747	-28.4
Reduction of Mn^{4+}		
$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	+0.526	-23.3
Reduction of Fe^{3+}		
$Fe(OH)_3 + 3H^+ + e^- \rightarrow Fe^{2+} + 3H_2O$	-0.047	-10.1
Reduction of SO_4^{2-}		
$SO_4^{2-} + 10H^+ + 8e^- \rightarrow H_2S + 4H_2O$	-0.221	-5.9
Reduction of CO_2		
$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$	-0.244	-5.6

