Technical Assistance
HYDROLOGY PROJECT

World Bank & Government of The Netherlands funded

Training module # WQ - 30

# *Advanced aquatic chemistry: Redox equilibria*

New Delhi, January 2000

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with
HALCROW, TAHAL, CES, ORG & JPS

# *Table of contents*

# 1. Module context

This module discusses redox equilibria relationships significant to characterisation of natural waters. Modules in which prior training is required to complete this module successfully and other, available related modules are listed in the table below.

While designing a training course, the relationship between this module and the others, would be maintained by keeping them close together in the syllabus and place them in a logical sequence. The actual selection of the topics and the depth of training would, of course, depend on the training needs of the participants, i.e. their knowledge level and skills performance upon the start of the course.

| No. | Module title | Code | Objectives |
|---|---|---|---|
| **1.** | Basic chemistry concepts | **WQ - 02** | • Convert units from one to another<br>• Discuss the basic concepts of quantitative chemistry<br>• Report analytical results with the correct number of significant digits. |
| **2.** | Understanding the hydrogen ion concentration (pH) | **WQ - 06** | • Discuss about the concept of pH<br>• Calculate pH |
| **3.** | The chemistry of dissolved oxygen measurement | **WQ - 11** | • Appreciate significance of DO measurement.<br>• Understand the chemistry of DO measurement by Winkler method. |
| **4.** | Understanding chemical oxygen demand test | **WQ - 18** | • Appreciate significance of COD measurement<br>• Understand the chemistry of COD measurement |
| **5.** | Basic aquatic chemistry concepts | **WQ - 24** | • Understand equilibrium chemistry and ionisation constants.<br>• Understand basis of pH and buffers<br>• Calculate different types of alkalinity. |
| **6.** | Advanced aquatic chemistry: solubility equilibria | **WQ - 29** | • Explain the principles of chemical equilibrium<br>• Define solubility product and explain how this relates to water quality assessment<br>• Define the octanol-water partition coefficient and explain how this relates to water quality assessment. |

# 2. Module profile

**Title** : Advanced aquatic chemistry: Redox equilibria

**Target group** : HIS function(s): Q2, Q3, Q5, Q6

**Duration** : One session of 75 min

**Objectives** : After the training the participants will be able to:

- Understand the principles of redox reactions
- Understand the significance of redox potential measurement

**Key concepts** :

- Galvanic cells
- Electrode potentials
- Stability field diagrams

**Training methods** : Lecture, exercises

**Training tools required** : Board, flipchart, OHS

**Handouts** : As provided in this module

**Further reading and references** :

- Chemistry for environmental engineers, C. N. Sawyer, P. L. McCarty & G. F. Parkin, Mc Graw Hill, Inc., 1994
- Process chemistry for water and wastewater treatment, L. D. Benefield, J. P. Judkins & B. L. Weand, Prentice-Hall, Inc., 1982

# 3. Session plan

| No | Activities | Time | Tools |
|---|---|---|---|
| 1 | ***Preparations:*** | | |
| 2 | ***Introduction:***<br>• Ask participants to differentiate between different types of chemical reactions<br>• Recapitulate reduction and oxidation reactions in the previous modules | 10 min | OHS |
| 3. | ***Galvanic Cell:***<br>• Describe component of a galvanic cell<br>• Explain the arrangement for study of a galvanic cell<br>• Explain standard hydrogen electrode and standard electrode potential. | 15 min | OHS |
| 4. | ***Nernst equation and cell potential***<br>• Explain how to write Nernst equation<br>• Define cell potential<br>• Explain how to calculate eqilibrium constant | 10 min | OHS |
| 5. | ***Stability field diagrams***<br>• Define redox potential<br>• Discuss relation between Eh and pH<br>• Explain construction and use of stability field diagrams | 15 min | OHS |
| 6. | ***Exercise*** | 15 min | Additional handout |
| 7. | ***Wrap out and evaluation*** | 10 min | |

# 4. Overhead/flipchart master

OHS format guidelines

| Type of text | Style | Setting |
|---|---|---|
| Headings: | OHS-Title | Arial 30-36, with bottom border line (not: underline) |
| Text: | OHS-lev1<br>OHS-lev2 | Arial 24-26, maximum two levels |
| Case: | | Sentence case. Avoid full text in UPPERCASE. |
| Italics: | | Use occasionally and in a consistent way |
| Listings: | OHS-lev1<br>OHS-lev1-Numbered | Big bullets.<br>Numbers for definite series of steps. Avoid roman numbers and letters. |
| Colours: | | None, as these get lost in photocopying and some colours do not reproduce at all. |
| Formulas/Equations | OHS-Equation | Use of a table will ease horizontal alignment over more lines (columns)<br>Use equation editor for advanced formatting only |

# Reduction - Oxidation Equilibria

- Theory of redox reaction
- Equilibrium state
- Stability field diagram

# Recapitulate

- DO & COD determination
- Reduction and oxidation proceed simultaneously
- Gain and loss of electrons
- Change in oxidation state or oxidation number

# Galvanic Cell (1)

- Half-reaction
  - *oxidation* $Zn(s) \leftrightharpoons Zn^{2+} + 2e$
  - *reduction* $Cu^{2+} + 2e \leftrightharpoons Cu(s)$
  - *overall* $Zn(s) + Cu^{2}+ \leftrightharpoons Zn^{2+} + Cu(s)$
- Flow of electrons can be monitored
  - *reactions should be separated*

# Galvanic Cell (2)

$\mathbf{Zn(s) \leftrightarrow Zn^{2+} + 2e}$

$\mathbf{Cu^{2+} + 2e \leftrightarrow Cu(s)}$

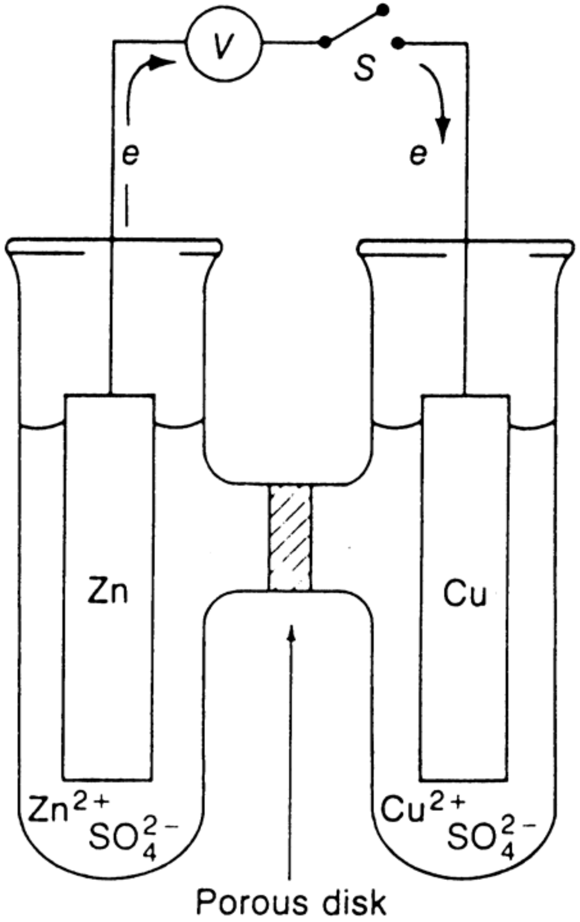

**Figure 1 Galvanic cell**

# Galvanic Cell (3)

- Electrodes, anode and cathode
  - *two half-cells*
- Arrangement for migration of ions
- External conductor for flow of electrons

# Electrode potential

- Potential developed at an electrode can be measured against reference electrode
- Reference hydrogen electrode
  - $2H^+ + 2e \leftrightharpoons H_2(g)$
  - *Acts as cathode or anode*
  - *Potential 0.0v*

# Standard Electrode Potential (1)

**$H_2(g) \leftrightarrow 2H^+ + 2e$**

**$Cu^{2+} + 2e \leftrightarrow Cu(s)$**

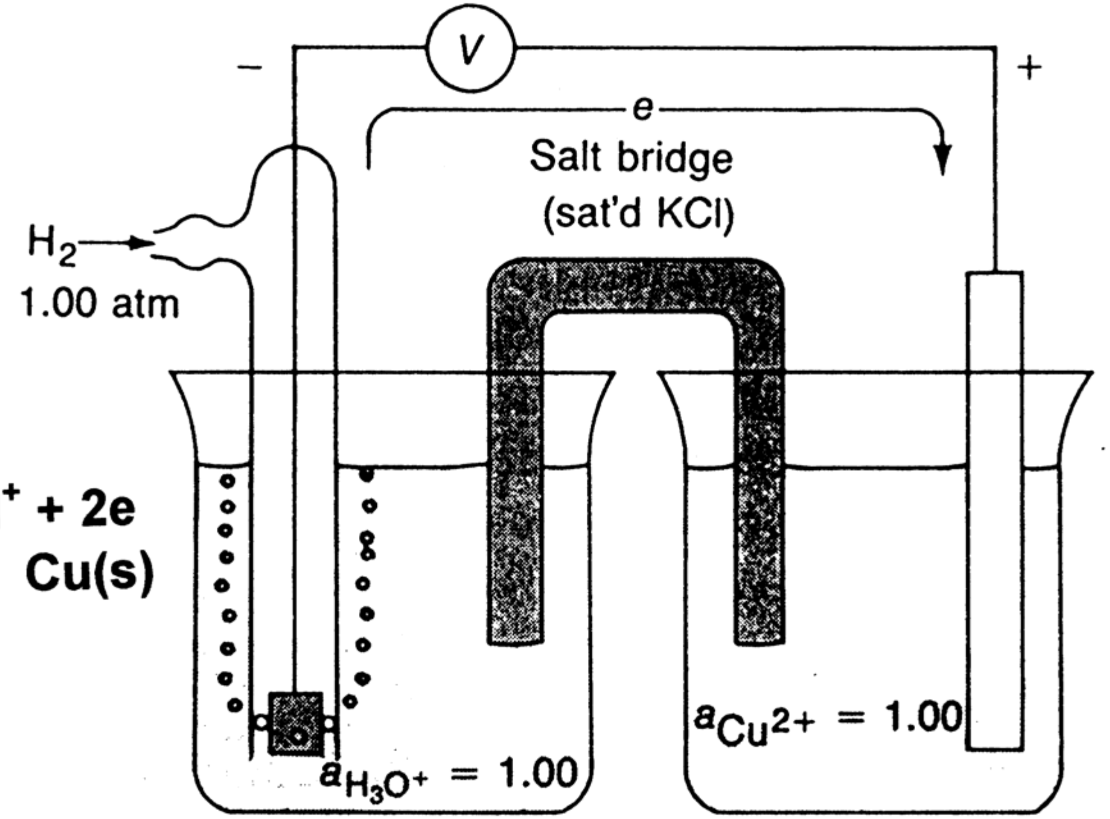

**Figure 2  Standard electrode potential definition**

# Standard Electrode Potential (2)

- All species in the two half-cells are at standard state
  - *P = 1atm, activities = 1*
  - *Flow of electrons from* $H_2$ *to Cu*
  - $E^0_h = +0.334V$
- For Zn /$H_2$ cell
  - *Flow of electrons from Zn to* $H_2$
  - $H_2$ *electrode becomes cathode*
  - $E^0_h = -0.763V$

# Standard Electrode Potential (3)

$O_2(g) + 4H^+ + 4e \leftrightharpoons 2H_2O + 1.229\ V$

$Cu^2 + 2e \leftrightharpoons Cu(s) + 0.337\ V$

$2H^+ + 2e \leftrightharpoons H_2(g) \quad 0.000\ V$

$Zn^{2+} + 2e \leftrightharpoons Zn(s)\ - 0.763\ V$

- Half-reaction always written as reduction
- Oxygen most effective electron acceptor in natural enviroment

# Nernst Equation

aA + bB + … + ne $\leftrightharpoons$ cC + dD + …

$$E_h = E_h^0 - \frac{0.0591}{n}\log\frac{[C]^c[D]^d...}{[A]^a[B]^b...},\ \text{at } 25^0\,C$$

- Gives potential when activities are not 1
- For standard conditions $E_h = E^0{}_h$

# Nernst Equation: Example

$Zn^{2+} + 2e \leftrightharpoons Zn(s)$

$$E_h = E_h^0 - \frac{0.0591}{n} \log \frac{[Zn(s)]}{[Zn^{2+}]}$$

$E^0_h = -0.763$,  $n = 2$,  $[Zn(s)] = 1$

$$E_h = -0.763 - 0.0285 \log \frac{1}{[Zn^{2+}]}$$

# Cell Potential

- Ordinarily hydrogen reference cell is not used.
- Any two half-reactions can be combined
- $E_{cell} = E_{cathode} - E_{anode}$
- Recognise cathode (+) and anode (-) on the basis of $E^0_h$ values or E values when standard conditions do not prevail.

# Equilibrium Constant

- Zn - Cu Cell
  - *Cu electrode acts as cathode,* $E^0_{Cu} > E^0_{Zn}$

$$E_{cell} = \left\{ E^0_{Cu} - \frac{0.059}{2} \log \frac{1}{\left[ Cu^{2+} \right]} \right\} - \left\{ E^0_{Zn} - \frac{0.059}{2} \log \frac{1}{\left[ Zn^{2+} \right]} \right\}$$

- At equilibrium, $E_{cell} = 0$

$$\log \frac{\left[ Zn^{2+} \right]}{\left[ Cu^{2+} \right]} = \frac{2\left( E^0_{Cu} - E^0_{zn} \right)}{0.0591} = \log K_{eq}$$

# Redox Potential

- At equilibrium all half-cell potentials are equal.
- $E_{Zn} = E_{cu} = E_{system}$ (redox potential)
- Potential of an inert electrode against a reference electrode
- $E_h$ (system)
  - *Oxidising environment ~ +0.3V*
  - *Reducing environment ~ -0.5V*

# Stability Field Diagram (1)

- Often redox reactions include $H^+$ or $OH^-$

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

- $E_h$, pH and predominant chemical species can be related

$$E_h = E_h^0 - 0.074pH - \frac{0.0591}{8}\log\frac{[H_2S]}{[SO_4^{2-}]}$$

- When $[H_2S] = [SO_4^{2-}]$

$$E_h = 0.3 - 0.074pH$$

# Stability Field Diagram (2)

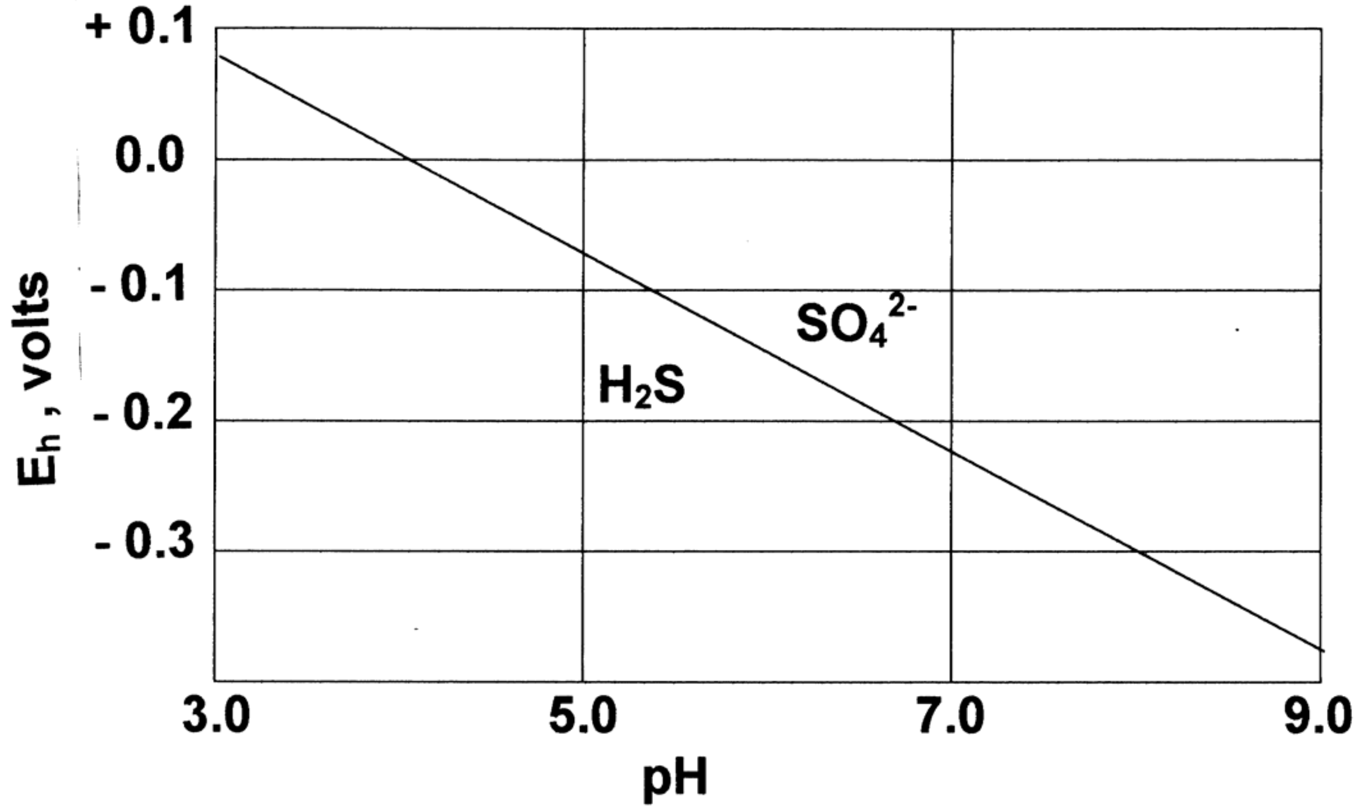

**Figure 3 $E_h$-pH diagram for sulphur species**

# Stability Field Diagram (3)

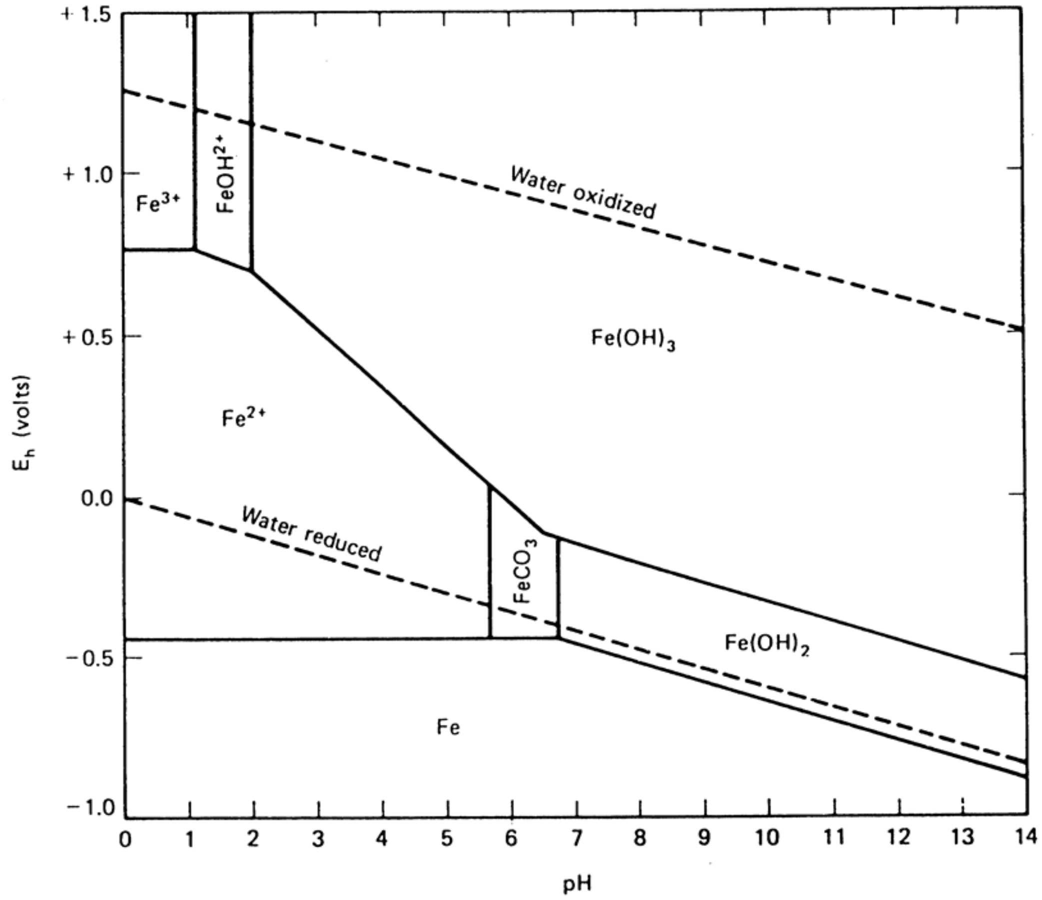

**Figure 4 $E_h$ vs pH diagram for iron system**

# 5. Evaluation sheets

# 6. Handout

## Reduction - Oxidation Equilibria

- Theory of redox reaction
- Equilibrium state
- Stability field diagram

## Recapitulate

- DO & COD determination
- Reduction and oxidation proceed simultaneously
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## Galvanic Cell (1)

- Half-reaction
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## Galvanic Cell (3)

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## Electrode potential

- Potential developed at an electrode can be measure against reference electrode
- Reference hydrogen electrode
    - $2H^{+} + 2e \leftrightharpoons H_2(g)$
    - *Acts as cathode or anode*
    - *Potential 0.0v*

## Standard Electrode Potential (2)

- All species in the two half-cell are at standard state
    - *P = 1atm, activities = 1*
    - *Flow of electrons from* $H_2$ *to Cu*
    - $E^{0}_{h} = +0.334V$
- For Zn /$H_2$ cell
    - *Flow of electrons from Zn to* $H_2$
    - $H_2$ *electrode becomes cathode*
    - $E^{0}_{h} = -0.763V$

## Standard Electrode Potential (3)

$O_2(g) + 4H^+ + 4e \leftrightharpoons 2H_2O + 1.229V$
$Cu^{2} + 2e \leftrightharpoons Cu(s) + 0.337V$
$2H^+ + 2e \leftrightharpoons H_2(g) \quad 0.000V$
$Zn^{2+} + 2e \leftrightharpoons Zn(s) \ - 0.763V$

- Half-reaction always written as reduction
- Oxygen most effective electron acceptor in natural environment

## Nernst Equation

$aA + bB + \ldots + ne \leftrightharpoons cC + dD + \ldots$

- Gives potential when activities are not 1

$$E_h = E_h^0 - \frac{0.0591}{n}\log\frac{[C]^c[D]^d\ldots}{[A]^a[B]^b\ldots},\ \text{at } 25^0\,C$$

- For standard conditions $E_h = E^0_h$

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$Zn^{2+} + 2e \leftrightharpoons Zn(s)$

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$E^0_h = -0.763$, $n = 2$, $[Zn(s)] = 1$

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## Cell Potential

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  - *Cu electrode acts as cathode, $E^0_{Cu} > E^0_{Zn}$*

$$E_{cell} = \left\{E^0_{Cu} - \frac{0.059}{2}\log\frac{1}{[Cu^{2+}]}\right\} - \left\{E^0_{Zn} - \frac{0.059}{2}\log\frac{1}{[Zn^{2+}]}\right\}$$

- At equilibrium, $E_{cell} = 0$

$$\log\frac{[Zn^{2+}]}{[Cu^{2+}]} = \frac{2\left(E^0_{Cu} - E^0_{zn}\right)}{0.0591} = \log K_{eq}$$

## Redox Potential

- At equilibrium all half-cell potentials are equal.
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## Stability Field Diagram (1)

- Often redox reactions include $H^+$ or $OH^-$

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

- $E_h$, pH and predominant chemical species can be related

$$E_h = E_h^0 - 0.074\text{pH} - \frac{0.0591}{8}\log\frac{[H_2S]}{[SO_4^{2-}]}$$

- When $[H_2S] = [SO_4^{2-}]$

  $E_h = 0.3 - 0.074\text{pH}$

**Add copy of Main text in chapter 8, for all participants.**

# 7. Additional handout

These handouts are distributed during delivery and contain test questions, answers to questions, special worksheets, optional information, and other matters you would not like to be seen in the regular handouts.

It is a good practice to pre-punch these additional handouts, so the participants can easily insert them in the main handout folder.

## Questions

1. **For each cell and given electrode reactions and standard potential, complete the following table.**

| Cell | Electrode reacions | $E^o_h$, V | Cathode | Cell potential, V |
|---|---|---|---|---|
| A. | $Cd^{2+} + 2e \leftrightharpoons Cd(s)$<br>$Ag^+ + e \leftrightharpoons Ag(s)$ | -0.403<br>+0.799 | | |
| B. | $H_2 + 2e \leftrightharpoons 2H^+$<br>$Cd + 2e \leftrightharpoons Cd(s)$ | 0.000<br>-0.403 | | |
| C. | $H_2 + 2e \leftrightharpoons 2H^+$<br>$Ag^+ + e \leftrightharpoons Ag(s)$ | 0.000<br>0.799 | | |

---

2. **A water sample contains both $Fe^{2+}$ and $Fe^{3+}$. If the pH = 7.5 and Eh = +0.25V. Using Figure 3, indicate which species will predominate.**

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## Questions and Answers

1. **For each cell and given electrode reactions and standard potential, complete the following table.**

| Cell | Electrode reacions | $E^o_h$, V | Cathode | Cell potential, V |
|---|---|---|---|---|
| A. | $Cd^{2+} + 2e \leftrightharpoons Cd(s)$<br>$Ag^+ + e \leftrightharpoons Ag(s)$ | -0.403<br>+0.799 | Ag | 1.202 |
| B. | $H_2 + 2e \leftrightharpoons 2H^+$<br>$Cd + 2e \leftrightharpoons Cd(s)$ | 0.000<br>-0.403 | H2 | 0.403 |
| C. | $H_2 + 2e \leftrightharpoons 2H^+$<br>$Ag^+ + e \leftrightharpoons Ag(s)$ | 0.000<br>0.799 | Ag | 0.7999 |

---

2. **A water sample contains both $Fe^{2+}$ and $Fe^{3+}$. If the pH = 7.5 and Eh = +0.25V. Using Figure 3, indicate which species will predominate.**

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$Fe^{3+}$

# 8. Main text

## Contents

# Advanced aquatic chemistry: Redox equilibria

## 1. Introduction

Chemical reactions can be divided into two groups: (a) reactions in which no change of oxidation state occurs, such as precipitation of calcium carbonate when sodium carbonate is added to water containing calcium ions, neutralisation of carbonate with acid or ionisation of acetic acid in water and (b) reactions in which changes in oxidation state of the reactants occurs.

Reduction-oxidation (redox) reactions are involved in the measurement of oxygen and chemical oxygen demand (see module # 11 and 18). Rules for balancing of redox reactions were also given in module # 18. This module discusses the basic theory of redox reactions and its applications in aqueous chemical systems.

## 2. Galvanic Cells

Redox reactions may be the result of direct transfer of electrons from donor to the acceptor. Recall that the loss of electrons from the donor results in its oxidation and the gain of electrons by the acceptor results in its reduction.

Thus, if metallic zinc is immersed in a copper sulphate solution the following reactions occur:

Oxidation : $Zn(s) \rightleftharpoons Zn^{2+} + 2e$ (1)

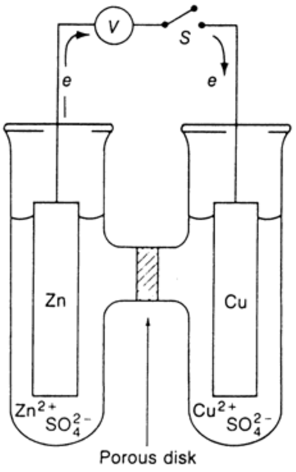
Reduction: $Cu^{2+} + 2e \rightleftharpoons Cu(s)$ (2)

------------------------------------------

Overall $Zn(s) + Cu^{2+} \rightleftharpoons Zn^{2+} + Cu(s)$ (3)

The individual oxidation and reduction reactions are called half-reactions, copper is deposited directly on solid zinc surface in the overall reaction.

The flow of electrons from Zn(s) to $Cu^{2+}$ can be monitored if the two half-reactions are physically isolated from each other. Such an arrangement is shown in Figure 1 and is called galvanic or electrochemical cell. The anode of the cell is the electrode at which oxidation occurs (Zn), while cathode is the electrode at which reduction takes place. The cell can be considered to comprise two half-cells.



$Zn(s) \leftrightarrow Zn^{2+} + 2e$

$Cu^{2+} + 2e \leftrightarrow Cu(s)$

**Figure 1 Galvanic cell**

## 2.1 Standard electrode potentials

It is obvious from Figure 1, that the potential of an electrode can be measured only against another half cell. An electrode potential is defined as the potential of a cell consisting of the electrode in question acting as cathode and a standard hydrogen electrode acting as anode.

Figure 2 illustrates a reference hydrogen electrode and a copper electrode for measurement of the electrode potential for the half-reaction given in Equation (2). Here instead of a porous disc, as in Figure 1, a salt bridge (a tube containing gelatin and saturated KCl) is provided to allow migration of negatively charged $SO^{=}_4$ from copper half cell and positively charged $H^+$ from hydrogen half cell to maintain electrical neutrality.

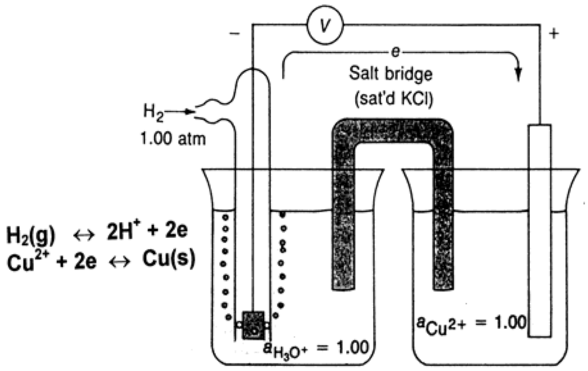


**Figure 2 Standard electrode potential definition**

The half reaction at the referene electrode is :

$$H_2(g) \leftrightharpoons 2H^+ + 2e \qquad (4)$$

Note that:

- All species in the standard half-cells are at standard state (P = 1 atm, activities = 1).
- The reference hydrogen half-cell is assigned a potential of 0.0V.
- Copper electrode bears a positive charge and it functions as cathode while the hydrogen electrode functions as anode.
- The cell develops a potential of 0.334V and by definition is assigned a positive sign. The standard electrode potential is, therefore, +0.334V.

Replacement of $Cu$-$Cu^{2+}$ half-cell with Zn electrode immersed in a solution with a $Zn^{2+}$ activity of one results in a potential of 0.763V. However, in this case the Zn electrode acts as anode. The half-reactions become:

$$Zn(s) \leftrightharpoons Zn^{2+} + 2e \qquad (5)$$

$$2H^+ + 2e \leftrightharpoons H_2(g) \qquad (6)$$

Since the hydrogen electrode acts as cathode, the electrode potential is assigned a negative sign and is equal to -0.763V.

Table 1 lists a few standard electrode potentials for the purpose of illustration. A more complete list may be obtained from chemistry handbooks.

Half-reactions for standard electrode potential are always written as reductions. A negative sign of the numerical value of the potential signifies that the half-reaction when coupled with the hydrogen reference electrode would be an oxidation reaction.

**Table 1 Standard electrode potentials, $E^o_h$ at $25^0C$**

| **Half-reactions** | **V** |
|---|---|
| $O_2(g) + 4H^+ + 4e \leftrightharpoons 2H_2O$ | + 1.229 |
| $Fe^{3+} + e \leftrightharpoons Fe^{2+}$ | + 0.771 |
| $Cu^{2+} + 2e \leftrightharpoons Cu(s)$ | + 0.337 |
| $SO_4^{2-} + 10H^+ + 8e \leftrightharpoons H_2S + 4H_2O$ | + 0.3 |
| $2H^+ + 2e \leftrightharpoons H_2(g)$ | 0.000 |
| $Cd^{2+} + 2e \leftrightharpoons Cd(s)$ | - 0.403 |
| $Zn^{2+} + 2e \leftrightharpoons Zn(s)$ | - 0.763 |

Entries in the table are according to the numerical values of the $E^0_h$. Among the listed reactions oxygen is the most effective electron acceptor.

## 2.2 The Nernst equation

For the generalised raversible half-reaction

$$aA + bB + \ldots + ne \leftrightharpoons cC + dD + \ldots \qquad (7)$$

where capital letters represents formulas for species, e is electron and a,b,c,d and n are number of moles, the potential $E_h$ is given by

$$E_h = E^o_h - \frac{RT}{nF} \ln \frac{[C]^c[D]^d\ldots}{[A]^a[B]^b\ldots} \qquad (8)$$

where

$E^o_h$ = standard electrode potential, V
R = gas constant, 8.316 $J.K^{-1}.mol^{-1}$
T = temperature, 298K ($25^oC$)
F = the faraday, 96487 coulombs
ln = the base for natural logarithms = 2.303 $\log_{10}$

Substitution of numerical values gives:

$$E_h = E^o_h - \frac{0.591}{2} \log \frac{[C]^c[D]^d\ldots}{[A]^a[B]^b\ldots} \qquad (9)$$

(The subscripts **h** indicate that the potential measurements are against hydrogen reference electrode).

**Example 1:**

Generate Nernst expression for the half-reaction $Zn^{2+}$ + 2e $\leftrightharpoons$ Zn(s)

The Nernst expression is:

$$E_h = E_h^o - \frac{0.591}{2}\log\frac{1}{\left[Zn^{2+}\right]}$$

The activity of elemental Zn(s) is unity. The electrode potential varies with the logarithm of reciprocal of molar $Zn^{2+}$ concentration, assuming that the activity = molar concentration.

## 2.3 Cell potential

The potential of an elctrochemical cell is obtained by combining the electrode potentials of the two half cell processes.

$$E_{cell} = E_{cathode} - E_{anode} \tag{10}$$

**Example 2:**

Calculate the cell potential for the cell shown in Figure 1. Assume that the reactants are at standard condition.

The standard electrode potentials for the Cu and Zn half-cells from Table 1 are +0.337 and -0.763V, respectively. Since $E^o_h$ value for Cu is higher it will act as cathode.

Therefore, $E_{cell}$ = +0.337 - (-0.763) = 1.100V

In Example 2, $E_{cell}$ may be written as $E^o_{cell}$, the standard cell potential, since $E^o_h$ values were used in determining the cell potential. In case the reactants are not at standard condition, the $E_h$ values can be calculated using the Nernst expression.

**Example 3:**

Calculate cell potential for the cell shown in Figure 1 when the activities of $Zn^{2+}$ and $Cu^{2+}$ are 0.1 and 0.01 mol/L.

The potential for Zn electrode is given by

$$E_{Zn} = -0.763 - \frac{0.0591}{2}\log\frac{1}{10^{-1}} = -0.793V$$

The potential for Cu electrode will be

$$E_{Cu} = -0.337 - \frac{0.0591}{2}\log\frac{1}{10^{-2}} = +0.278V$$

Therefore, the cell potential will be

$$E_{cell} = +0.278 - (-0.793) = 1.071V$$

# 3. Equilibrium state

## 3.1 Equilibrium constant

As a redox reaction proceeds, the concentration of the reactants decrease. Simultaneously the concentrations of products increase. In a galvanic cell, the potential decreases and ultimately at equilibrium it becomes zero. Thus,

$$E_{cell} = 0 = E_{cathode} = E_{anode} \tag{11}$$

Taking the example of Zn - Cu cell, therefore at equilibrium:

$$E_{Cu} - E_{Zn} = 0$$

or $$E^0_{Cu} - \frac{0.0591}{2}\log\frac{1}{\left[Cu^{2+}\right]} - E^0_{Zn} + \frac{0.0591}{2}\log\frac{1}{\left[Zn^{2+}\right]} = 0$$

or $$\frac{2\left(E^0_{Cu} - E^0_{Zn}\right)}{0.0591} = \log\frac{\left[Zn^{2+}\right]}{\left[Cu^{2+}\right]} = \log K_{eq} \tag{12}$$

where $K_{eq}$ is the equilibrium constant for the overall reaction, Equation 3.

Note that the concentrations Equation (12) would be the equilibrium concentrations. The value of $K_{eq}$ can be calculated by substituting the values of standard potentials in the equation.

## 3.2 Redox potential

In an aqueous chemical system there may be a number of chemical species giving rise to corresponding half-reactions. Each half-reaction would develop a half-cell potential whose magnitude would depend on the standard electrode potential for the half-reaction and the activities of relevant species and temperature. If the chemical system is at equilibrium (analogue to zero potential of a galvanic cell), these potentials are equal.

As an example, a natural water may be at equilibrium with respect to the following half-reactions:

$$Fe^{3+} + e \leftrightharpoons Fe^{++} \text{ and } SO_4^{2-} + 10H^+ + 8e \leftrightharpoons H_2S + 4H_2O$$

Therefore, $E_{Fe} = E_S = E_{system}$

The potential of the system is called the redox potential. It is determined by immersing an inert electrode, usually platinum, in the chemical system in question and determining the potential difference with respect to hydrogen or other reference electrode of known potential.

**Example 4:**

The redox potential of a sample of water containing $Fe^{2+}$ and $Fe^{3+}$ ions is 0.5volt. Which is the predominant specie of iron?

Write the Nernst expression for $Fe^{3+} + e \leftrightharpoons Fe^{2+}$

$$E_h = 0.5 = 0.77 - \frac{0.0591}{1}\log\frac{\left[Fe^{2+}\right]}{\left[Fe^{3+}\right]}$$

or $$\log\frac{\left[Fe^{2+}\right]}{\left[Fe^{3+}\right]} = \frac{0.27}{0.0591} = 4.58$$

or $$\log\frac{\left[Fe^{2+}\right]}{\left[Fe^{3+}\right]} = 10^{4.58}$$

Therefore, $Fe^{2+}$ dominates

## 3.3 Stability field diagrams

Many of the redox reactions include $H^+$ or $OH^-$ ions. Stability diagrams can be drawn to describe the relationship between $E_h$(cell potential with respect to hydrogen electrode), pH and stable chemical species for a particular chemical system.

For example, the ability of a natural environment to oxidise sulphur will vary with its redox potential. Sea water at the surface, where it is undergoing aeration, may have a potential of +0.3 volt contains sulphates, while near the bottom sediments in presence of organic sediments, the potential may be -0.5volt and sulphides may be present. The relevant half-reaction relating the oxidised specie of sulphur, $SO_4^{2-}$, to the reduced specie, $H_2S$, is:

$$SO^{2-}_4 + 10H^+ + 8e \leftrightharpoons H_2S + 4H_2O \tag{13}$$

Writing the Nernst expression for the above equation relation between $E_h$ and pH is obtained:

$$E_h = E_h^0 - \frac{0.0591}{8}\log\left\{\frac{\left[H_2S\right]}{\left[SO_4^{2-}\right]}\cdot\frac{1}{\left[H^+\right]^{10}}\right\}$$

or $$E_h = E_h^0 - 0.074pH - \frac{0.0591}{8}\log\frac{\left[H_2S\right]}{\left[SO_4^{2-}\right]} \tag{14}$$

Assuming that the ratio of $[H_2S]$ and $[SO_4^{2-}]$ is one and substituting the value of $E^0_h$ from Table 1

$$E_h = 0.3 - 0.074pH \tag{15}$$

A plot of Equation (15) is shown in Figure 3. If the $E_h$ and pH value of a chemical system plot on this line both the species ($H_2S$ and $SO_4^{2-}$) have the same concentration. However, if for example the $E_h$ value is 0.1 and the pH is 7, which is a point on the right side of the plot, substitution of these values in Equation (14) gives the value of ration $[H_2S] / [SO_4^{2-}] = 10^{-43}$. Therefore, the plotting positions on the right side of the line show a predominance of $SO_4^{2-}$ species in the water.

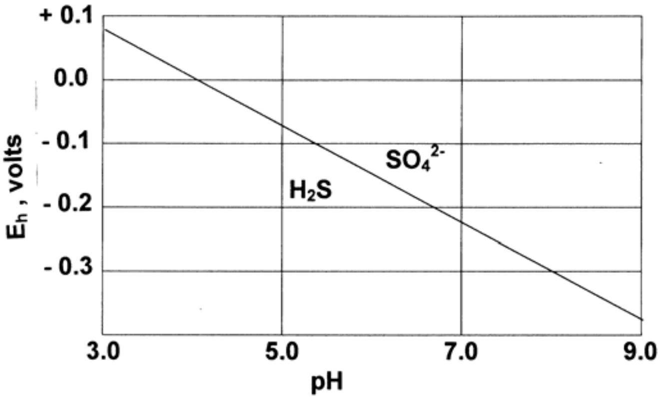


Figure 3 $E_h$-pH diagram for sulphur species

The first step in constructing a stability field diagram is to identify the pertinent reactions. The reactions may not be limited to only redox reactions. The plotting equations are then developed. Unit activities may be assumed for all soluble species.

Figure 4 shows a stability field diagram for iron. Iron species form various hydroxides and also react with carbonate. These reactions are therefore included. The concentration of total carbonic species is assumed as $10^{-5}$M.

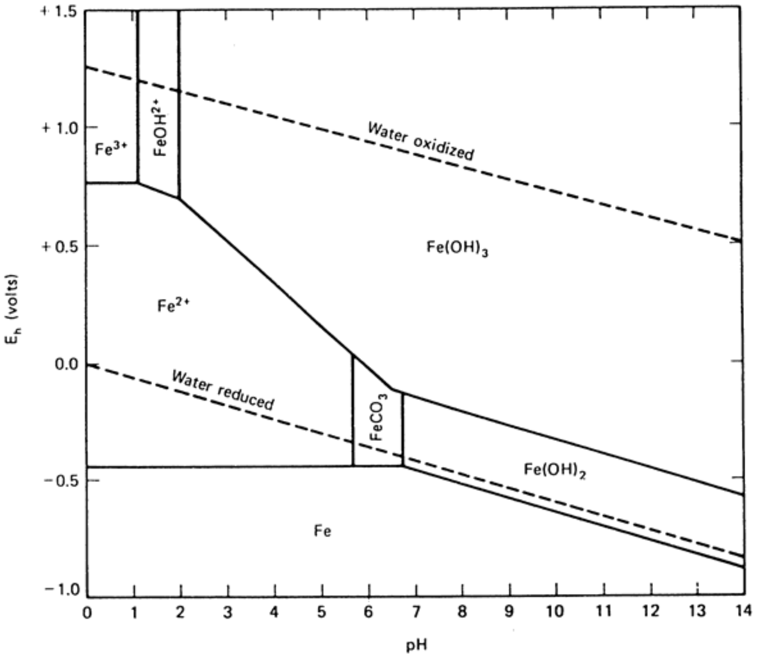


Figure 4 $E_h$ vs pH diagram for iron system

The diagram also shows the theroretical limits for $E_h$ and pH in nature. The strongest oxidising agent commonly found in nature is the oxygen of the atmosphere. The upper limit is given by the half-reaction:

$$O_2 + 4H^+ + 4e \leftrightharpoons 2H_2O \qquad (16)$$

and its plotting equation is:

$$E_h = 12.2. - 0.59 \text{ pH} \qquad (17)$$

The lower limit is given by the Nernst expression for Equation (6).

$$E_h = -0.059 \text{ pH} \qquad (18)$$

The diagram shows that the change from Fe(II) to Fe(III) falls approximately in the middle of the field representing conditions in nature, $E_h$ - 0.2 to + 0.8 volt and pH 2 to 10. Shifts in pH or $E_h$ of the environment changes one form to the other. Reduced iron compounds occur in sediment layers where $E_h$ may be low. The diagram also indicates that oxidation of iron takes place more completely under alkaline conditions.