P10 Elektrokemija

TABLE 21.1 Standard Reduction Potentials in Aqueous Solution at 25 °C*

Reduction Half-Reaction			$E°$ (V)
$F_2(g) + 2\ e^-$	$\longrightarrow$	$2\ F^-(aq)$	+2.87
$H_2O_2(aq) + 2\ H_3O^+(aq) + 2\ e^-$	$\longrightarrow$	$4\ H_2O(\ell)$	+1.77
$PbO_2(s) + SO_4^{2-}(aq) + 4\ H_3O^+(aq) + 2\ e^-$	$\longrightarrow$	$PbSO_4(s) + 6\ H_2O(\ell)$	+1.685
$MnO_4^-(aq) + 8\ H_3O^+(aq) + 5\ e^-$	$\longrightarrow$	$Mn^{2+}(aq) + 12\ H_2O(\ell)$	+1.52
$Au^{3+}(aq) + 3\ e^-$	$\longrightarrow$	$Au(s)$	+1.50
$Cl_2(g) + 2\ e^-$	$\longrightarrow$	$2\ Cl^-(aq)$	+1.360
$Cr_2O_7^{2-}(aq) + 14\ H_3O^+(aq) + 6\ e^-$	$\longrightarrow$	$2\ Cr^{3+}(aq) + 21\ H_2O(\ell)$	+1.33
$O_2(g) + 4\ H_3O^+(aq) + 4\ e^-$	$\longrightarrow$	$6\ H_2O(\ell)$	+1.229
$Br_2(\ell) + 2\ e^-$	$\longrightarrow$	$2\ Br^-(aq)$	+1.08
$NO_3^-(aq) + 4\ H_3O^+(aq) + 3\ e^-$	$\longrightarrow$	$NO(g) + 6\ H_2O(\ell)$	+0.96
$OCl^-(aq) + H_2O(\ell) + 2\ e^-$	$\longrightarrow$	$Cl^-(aq) + 2\ OH^-(aq)$	+0.89
$Hg^{2+}(aq) + 2\ e^-$	$\longrightarrow$	$Hg(\ell)$	+0.855
$Ag^+(aq) + e^-$	$\longrightarrow$	$Ag(s)$	+0.80
$Hg_2^{2+}(aq) + 2\ e^-$	$\longrightarrow$	$2\ Hg(\ell)$	+0.789
$Fe^{3+}(aq) + e^-$	$\longrightarrow$	$Fe^{2+}(aq)$	+0.771
$I_2(s) + 2\ e^-$	$\longrightarrow$	$2\ I^-(aq)$	+0.535
$O_2(g) + 2\ H_2O(\ell) + 4\ e^-$	$\longrightarrow$	$4\ OH^-(aq)$	+0.40
$Cu^{2+}(aq) + 2\ e^-$	$\longrightarrow$	$Cu(s)$	+0.337
$Sn^{4+}(aq) + 2\ e^-$	$\longrightarrow$	$Sn^{2+}(aq)$	+0.15
$2\ H_3O^+(aq) + 2\ e^-$	$\longrightarrow$	$H_2(g) + 2\ H_2O(\ell)$	0.00
$Sn^{2+}(aq) + 2\ e^-$	$\longrightarrow$	$Sn(s)$	−0.14
$Ni^{2+}(aq) + 2\ e^-$	$\longrightarrow$	$Ni(s)$	−0.25
$V^{3+}(aq) + e^-$	$\longrightarrow$	$V^{2+}(aq)$	−0.255
$PbSO_4(s) + 2\ e^-$	$\longrightarrow$	$Pb(s) + SO_4^{2-}(aq)$	−0.356
$Cd^{2+}(aq) + 2\ e^-$	$\longrightarrow$	$Cd(s)$	−0.40
$Fe^{2+}(aq) + 2\ e^-$	$\longrightarrow$	$Fe(s)$	−0.44
$Zn^{2+}(aq) + 2\ e^-$	$\longrightarrow$	$Zn(s)$	−0.763
$2\ H_2O(\ell) + 2\ e^-$	$\longrightarrow$	$H_2(g) + 2\ OH^-(aq)$	−0.8277
$Al^{3+}(aq) + 3\ e^-$	$\longrightarrow$	$Al(s)$	−1.66
$Mg^{2+}(aq) + 2\ e^-$	$\longrightarrow$	$Mg(s)$	−2.37
$Na^+(aq) + e^-$	$\longrightarrow$	$Na(s)$	−2.714
$K^+(aq) + e^-$	$\longrightarrow$	$K(s)$	−2.925
$Li^+(aq) + e^-$	$\longrightarrow$	$Li(s)$	−3.045

Increasing strength of oxidizing agents ↑

Increasing strength of reducing agents ↓

Električno delo je mogoče izračunati, če izmerimo napetost galvanskega člena (E):

$$A_{el.} = zFE$$

F…….9.65x10^4 J/V.mol (As)…… naboj 1mola ionov
z……število elektronov, ki jih reducent odda
Med napetostjo galv. člena in prosto entalpijo je naslednja zveza:

$$\Delta G^0 = -zFE^o$$

E^0 ..... je normalni potencial*
Zveza omogoča določevanje TD podatkov iz elektrokemijskih meritev.

Koncentracijsko odvisnost redoks potenciala podaja Nernstova enačba:

$$E = E^o + RT/zF \times \ln [oks]/[red]$$

$$E = E^o + 0{,}0257/z \times \ln [oks]/[red]$$

Pri kovinski elektrodi je koncentracija kovine konstantna, enačbo poenostavimo, [red] je konstanten.

$$E = E^o + RT/zF \times \ln [M^+]$$

Tudi pri standardni vodikovi elektrodi lahko upoštevamo, da je konc. vodika konstantna (to je pri konstantnem tlaku vodika):

$$E = E^o + RT/zF \times \ln [H^+]$$

25°C:

$E^o = 0$ za stand. vodikovo elektrodo; z=1

$E = 0{,}059 \log [H+]$

$E = -0{,}059$ pH

Zveza omogoča neposredno merjenje pH z vodikovo elektrodo!

Redoksipotenciali

- **Normalni redoksipotenciali so tabelirani. Izmerjeni so pri aktivnosti ionov 1.**
- **Redoksipotenciali so odvisni od koncentracij**
- $E = E^o + RT/zF \ln C_{oks} / C_{red}$
- **Redoksipotenciali** so merilo ali neka reakcija sploh poteče, če je :
- $\Delta E^o = E^o_{(oks)} - E^o_{(red)} > 0$
- **Reakcijo lahko ovirajo še drugi faktorji**
- **polarizacija elektrod**
- **mejni potencial**

EXAMPLE 21.6 *The Relation Between* E° *and* ΔG°_{rxn}

The reaction of zinc metal with copper(II) ions (see Figure 21.3) has a standard cell potential E° of +1.10 V at 25 °C. Calculate ΔG°_{rxn} for the reaction.

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

Solution To obtain ΔG°_{rxn} we substitute the given E° value into Equation 21.1.

$$\Delta G^\circ_{rxn} = -(2.00 \text{ mol electrons transferred})\left(\frac{9.65 \times 10^4 \text{ J}}{\text{V} \cdot \text{mol}}\right)(1.10 \text{ V})\left(\frac{1 \text{ kJ}}{1000 \text{ J}}\right)$$

$$= -212 \text{ kJ}$$

EXERCISE 21.4 *Electrochemical Cells*

A voltaic cell has been assembled with the net reaction

$$Ni(s) + 2\ Ag^{+}(aq) \longrightarrow Ni^{2+}(aq) + 2\ Ag(s)$$

Give the half-reactions for this electron transfer process, indicating whether each is an oxidation or reduction and deciding which happens at the anode and which at the cathode. What is the direction of electron flow in an external wire connecting the two electrodes? If a salt bridge connecting the cell compartments contains KNO_3, what is the direction of flow of the nitrate ions? ■

21.4. Oxidation at the anode: $Ni(S) \longrightarrow Ni^{2+}(aq) + 2e^-$

Reduction at the cathode: $e^- + Ag^+(aq) \longrightarrow Ag(s)$

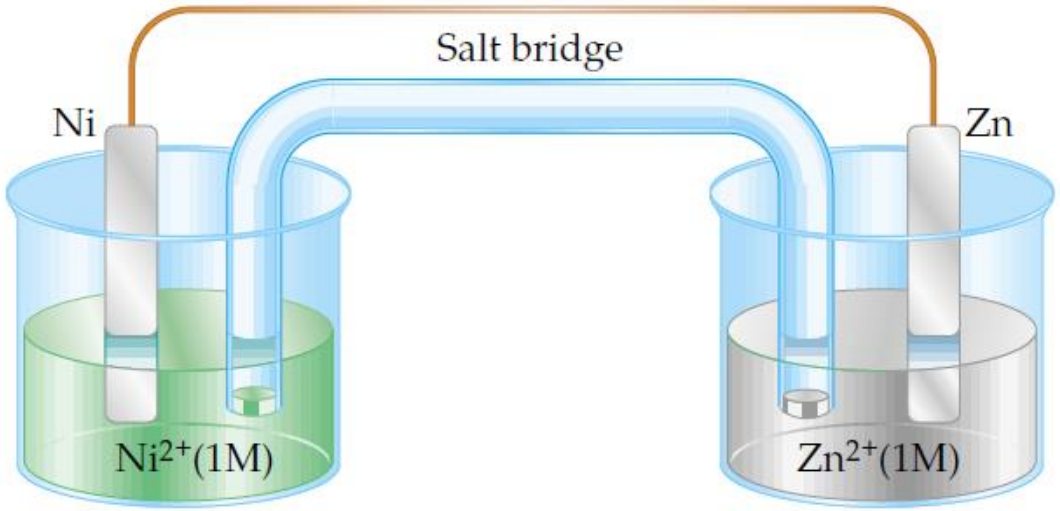
Electrons flow from the anode (Ni) to the cathode (Ag), and NO_3^- ions flow from the cathode compartment (containing a declining concentration of Ag^+) to the anode compartment (where there is an increasing concentration of Ni^{2+}).

EXAMPLE 21.7 *Determining a Half-Reaction Potential*

The cell illustrated here has a potential of $E° = +0.51$ V at 25 °C. The net ionic equation for the cell reaction is

$$Zn(s) + Ni^{2+}(aq, 1\ M) \longrightarrow Zn^{2+}(aq, 1\ M) + Ni(s)$$

Which electrode is the anode, and which is the cathode? What are the polarities of the electrodes? What is the value of $E°$ for the half-cell $Ni^{2+}(aq) + 2\ e^- \rightarrow Ni(s)$?



Solution $Zn(s)$ is oxidized to $Zn^{2+}(aq)$, so the Zn electrode is the anode and is negatively charged because it is the source of electrons. Nickel(II) ions are reduced to Ni metal at the Ni electrode, so this is the cathode, and it is positive.

Because the overall cell potential is known, and the potential for the $Zn(s)/Zn^{2+}(aq)$ half-cell is known, $E°$ for the nickel half-cell can be calculated.

Anode, oxidation:	$Zn(s) \longrightarrow Zn^{2+}(aq) + 2\ e^-$	$E° = +0.76\ V$
Cathode, reduction:	$Ni^{2+}(aq) + 2\ e^- \longrightarrow Ni(s)$	$E° = ?\ V$
Net reaction:	$Zn(s) + Ni^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Ni(s)$	$E°_{net} = +0.51\ V$

At 25 °C the value of $E°$ for the reaction $Ni^{2+}(aq) + 2\ e^- \rightarrow Ni(s)$ is -0.25 V.

EXAMPLE 21.8 *Predicting* E° *and the Direction of a Redox Reaction*

Decide if each of the following reactions is product-favored in the direction written, and calculate E°_{net}.

1. $2\ Al(s) + 3\ Sn^{4+}(aq) \longrightarrow 2\ Al^{3+}(aq) + 3\ Sn^{2+}(aq)$

2. $2\ Cl^{-}(aq) + Br_2(\ell) \longrightarrow 2\ Br^{-}(aq) + Cl_2(aq)$

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2. $2\ Cl^-(aq) + Br_2(\ell) \longrightarrow 2\ Br^-(aq) + Cl_2(aq)$

Solution Reaction (1) is predicted to be product-favored as written (and thus to have a positive E°). As indicated in Table 21.1, Al(s) is a stronger reducing agent than Sn^{2+}, and Sn^{4+} is a stronger oxidizing agent than Al^{3+}. This is verified by the positive value of E°.

$$\begin{array}{rll} 2\ [Al(s) \longrightarrow Al^{3+}(aq) + 3\ e^-] & & E^\circ = +1.66\ V \\ 3\ [Sn^{4+}(aq) + 2\ e^- \longrightarrow Sn^{2+}(aq)] & & E^\circ = +0.15\ V \\ \hline 2\ Al(s) + 3\ Sn^{4+}(aq) \longrightarrow 3\ Sn^{2+}(aq) + 2\ Al^{3+}(aq) & & E^\circ_{net} = +1.81\ V \end{array}$$

Reaction (2) is predicted to be reactant-favored. Based on the reduction potentials in Table 21.1, we know that Br_2 is a weaker oxidizing agent than Cl_2 and Cl^- is a weaker reducing agent than Br^-. The negative sign of E°_{net} for the reaction as written confirms this.

$$\begin{array}{rll} 2\ Cl^-(aq) \longrightarrow Cl_2(aq) + 2\ e^- & & E^\circ = -1.360\ V \\ Br_2(\ell) + 2\ e^- \longrightarrow 2\ Br^-(aq) & & E^\circ = +1.08\ V \\ \hline 2\ Cl^-(aq) + Br_2(aq) \longrightarrow 2\ Br^-(aq) + Cl_2(aq) & & E^\circ_{net} = -0.28\ V \end{array}$$

Uporaba Nernstove enačbe:

$$E = E^o + RT / zF \times \ln [oks] / [red]$$

$$E = E^o + 0{,}0257 / z \times \ln [oks] / [red]$$

EXAMPLE 21.10 *Using the Nernst Equation*

Determine the cell potential at 25 °C for

$$Fe(s) + Cd^{2+}(aq) \longrightarrow Fe^{2+}(aq) + Cd(s)$$

when (1) $[Fe^{2+}] = 0.010$ M and $[Cd^{2+}] = 1.0$ M and (2) $[Fe^{2+}] = 1.0$ M and $[Cd^{2+}] = 0.010$ M.

Solution To calculate a nonstandard potential, we first need the standard potential for the cell reaction, E°_{net}.

Oxidation:	$Fe(s) \longrightarrow Fe^{2+}(aq) + 2\ e^-$	$E^\circ = +0.44\ V$
Reduction:	$Cd^{2+}(aq) + 2\ e^- \longrightarrow Cd(s)$	$E^\circ = -0.40\ V$
Net reaction:	$Fe(s) + Cd^{2+}(aq) \longrightarrow Fe^{2+}(aq) + Cd(s)$	$E^\circ_{net} = +0.04\ V$

Next, let us substitute E° and the conditions for solution (1) into the Nernst equation.

$$E = E^\circ - \frac{0.0257\ V}{n} \ln \frac{[Fe^{2+}]}{[Cd^{2+}]}$$

As in chemical equilibrium calculations (see Chapter 16), the concentration of a solid does not enter into the expression. Now, using $n = 2$ (the number of moles of electrons transferred), and the ion concentrations given earlier,

$$E = +0.04\ V - \frac{0.0257\ V}{2} \ln \frac{0.010}{1.0} = +0.10\ V$$

The cell potential E is larger than E°_{net}, so the tendency to transfer electrons from $Fe(s)$ to $Cd^{2+}(aq)$ is greater than under standard conditions.

For the condition described by (2), the Nernst equation is

$$E = +0.04\ V - \frac{0.0257\ V}{2} \ln \frac{1.0}{0.010} = -0.02\ V$$

The cell potential E is larger than E°_{net}, so the tendency to transfer electrons from Fe(s) to $Cd^{2+}(aq)$ is greater than under standard conditions.

For the condition described by (2), the Nernst equation is

$$E = +0.04\ \text{V} - \frac{0.0257\ \text{V}}{2} \ln \frac{1.0}{0.010} = -0.02\ \text{V}$$

The cell potential E is now negative. This means the reaction, as originally written, is reactant-favored. Therefore, the reaction is product-favored in the other direction. Under these conditions, cadmium metal will reduce iron(II) ion.

$$Fe^{2+}(aq, 1.0\ \text{M}) + Cd(s) \longrightarrow Fe(s) + Cd^{2+}(aq, 0.010\ \text{M}) \qquad E_{net} = +0.02\ \text{V}$$

Faraday-ev zakon elektrolize

- množina snovi, ki je podvržena oksidaciji oz. redukciji na elektrodi med elektrolizo je sorazmerna množini električnega toka, ki steče skozi celico.
- izračun iz električnega naboja, porabljenega pri elektrolizi.
- 1 mol e^- lahko izloči iz raztopine, 1 mol enovalentne kovine ($M^+ + e^- = M$, z=1) ali 1/2 mola dvovalentne kovine ($M^{2+} + 2e^- = M$, z=2).
- Skupni naboj mola elektronov je 96485 As.
- 1 Faraday= 96485 C (A.s)= 26,8 Ah = 1mol e^- =
- $6.022 \times 10^{23} e^-$
- Električni tok izražamo v amperih(A).
- 1A=1C/s

1.Primer:

1g bakra izločimo iz raztopine bakrovega(II) sulfata(VI) z jakostjo toka 0,3A. Koliko časa je potrebno?

- $CuSO_4 = Cu^{2+} + SO_4^{2-}$

  K: $Cu^{2+} + 2e^- \rightarrow Cu\ (s)$ $I = 0,3A$

- 96487 As izloči iz raztopine 63,54g/2 (z=2)
- Cu
- potrebni naboj za 1g: 96485/31,77= 3037As, to je pri toku 0,3A;
- $t = Q/I$ 3037/0,3= 10123s= 2,8ur

- **2.Primer:**
- Kovinski Al lahko dobimo z elektrolizo AlF_3, raztopljenim v tekočem kriolitu: K_3AlF_6. Kakšno količina Al se izloči na katodi, če teče tok 5A, 4 ure?

$$\text{Current, } I \text{ (amps)} = \frac{\text{electric charge (coulombs, C)}}{\text{time (seconds, s)}}$$

Koliko gramov in litrov F_2 se zloči na anodi p.n.p. ?

m(Al) = ?
I = 5A
T = 4 h
Redukcija K^- : $Al^{3+} + 3e^- \rightarrow Al(s)$

$I \cdot t = 5A \cdot 4 \cdot 60 \cdot 60s = 72\,000\ As\ (C)$

96485 As - - - - - - mol Al/30= 27g/3
72000 As - - - - - - x
m = 6,71 g Al

Oksidacija A^+: $2F^- \rightarrow F_2 + 2\ e^-$

96485 As - - - - - - mol F_2/2= 19x2g/2
72000 As - - - - - - x
m = 14,17 g F_2 (0,372 mol)

V=Vm x n= 22,4Lx0,372 mol=8,36L F_2

EXAMPLE 21.13 *Using the Faraday Constant*

A current of 1.50 amp is passed through a solution containing silver ions for 15.0 min. The voltage is such that silver deposited at the cathode. What mass of silver, in grams, is deposited?

$$Ag^+(aq) + e^- \longrightarrow Ag(s)$$

Solution From the half-reaction we know that if 1 mol of electrons passed through the cell, then 1 mol of silver was deposited. To find the number of moles of electrons, we need to know the total electric charge passed through the cell. The charge can be calculated from experimental measurements of the current (in amps) and the time the current flowed. Thus, the logic of the calculation is

Time (s) × current (amps) → Charge, C → Mol e^- → Mol Ag → Mass A

1. Calculate the charge (number of coulombs) passed in 15.0 min.

$$\begin{aligned}\text{Charge (coulombs, C)} &= \text{current (amps)} \times \text{time (seconds)} \\ &= 1.50 \text{ amps } (15.0 \text{ min})(60.0 \text{ s/min}) \\ &= 1.35 \times 10^3 \text{ C}\end{aligned}$$

2. Calculate the number of moles of electrons.

$$1.35 \times 10^3 \text{ C}\left(\frac{1 \text{ mol } e^-}{9.65 \times 10^4 \text{ C}}\right) = 1.40 \times 10^{-2} \text{ mol } e^-$$

3. Calculate the number of moles of silver that passed through the cell and then the mass of silver deposited.

$$1.40 \times 10^{-2} \text{ mol } e^-\left(\frac{1 \text{ mol Ag}}{1 \text{ mol } e^-}\right)\left(\frac{107.9 \text{ g Ag}}{1 \text{ mol Ag}}\right) = 1.51 \text{ g Ag}$$

21.2 A Summary of Electrochemical Terminology

Whether you are describing a voltaic cell or an electrolysis cell, the terms *anode* and *cathode* always refer to the electrodes at which oxidation and reduction occur, respectively. The polarity of the electrodes is reversed, however, in a battery or electrolysis cell.

Type of Cell	Electrode	Function	Polarity
Battery	Anode	Oxidation	—
	Cathode	Reduction	+
Electrolysis	Anode	Oxidation	+
	Cathode	Reduction	—

In a voltaic cell, the negative electrode is the one at which electrons are produced. In an electrolysis cell, the negative electrode is the one onto which the external source is "pumping" the electrons. ■

EXAMPLE 21.12 *Electrolysis of Aqueous NaOH*

Predict what happens when an electric current is passed through aqueous sodium hydroxide.

Solution First, list all the species in solution. In this case they are Na^+, OH^-, and H_2O. Next, use Table 21.1 to decide which of the species can be oxidized and which can be reduced, and note the potential of each possible reaction.

Reductions:	$Na^+(aq) + e^- \longrightarrow Na(s)$	$E^\circ = -2.71\ V$
	$2\ H_2O(\ell) + 2\ e^- \longrightarrow H_2(g) + 2\ OH^-(aq)$	$E^\circ = -0.83\ V$
Oxidation:	$4\ OH^-(aq) \longrightarrow O_2(g) + 2\ H_2O(\ell) + 4\ e^-$	$E^\circ = -0.40\ V$

It is evident that water is reduced to H_2 at the cathode and OH^- is oxidized to O_2 at the anode. The cell reaction is $2\ H_2O(\ell) \rightarrow 2\ H_2(g) + O_2(g)$, and the potential under standard conditions is -1.23 V.

2.Primer:

Tok teče skozi 500 ml raztopine CaI_2. Naslednje reakcije potekajo:

- A^-: $2I^- \rightarrow I_2 + 2e^-$
- K^+: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

- Čez nekaj časa pokaže analiza raztopine, da se sprosti 47,7 mmol I_2.
- Koliko Faradayev naboja je steklo skozi raztopino?
- Kakšen volumen H_2 p.n.p se sprosti?
- Kakšen je pH raztopine?