Lecture General Chemistry
Winter Term 2023/24

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- Website (Slides, Excercises):
- http://www.chemie.uni-siegen.de/pc/lehre/nanoscitec/

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Acids and Bases

What are acids, what are bases?

Arrhenius: Acids release protons
Bases release hydroxid ions

Brønstedt: Acids: Proton donators
Bases: Proton akzeptors

some substances can do both: amphoteric substances

$H_2O \rightarrow H^+ + OH^-$

Autoprotolysis of water

$H_20 \leftrightarrow H^+ + OH^-$

$$K = \frac{c(\mathrm{H^+})c(\mathrm{OH^-})}{c(\mathrm{H_2O})}$$

if K ≠ 0, in pure water: $c\,(H^+) = c\,(OH^-) > 0$

Definition: Water is neutral (neither acidic nor basic) if $c\,(H^+) = c\,(OH^-)$

Determination: eg electrochemically: specify $c(OH^-)$, measure $c(H^+)$

$$K = \frac{c(\mathrm{H^+})c(\mathrm{OH^-})}{c(\mathrm{H_2O})}$$

(almost) constant, $c(H_2O)$ = 55,5 mol/L

$$c(\mathrm{H^+}) \cdot c(\mathrm{OH^-}) = K \cdot c(\mathrm{H_2O}) = K_w = 1{,}1 \cdot 10^{-14} \approx 10^{-14}\,\frac{\mathrm{mol^2}}{\mathrm{L^2}}$$

K_w : Ion product of water

Water at 25 °C is neutral if $c\,(H^+) = c\,(OH^-) = 10^{-7}$ mol/L

What about other temperatures?
(Le Chatelier /Braun)

T/°C	pH	T/°C	pH
0	7,47	30	6,92
10	7,27	37	6,81
20	7,08	50	6,63
25	7,00	100	6,13

pH, pOH and pK_A

$$pH = -\lg c(H^+) \qquad pOH = -\lg c(OH^-) \qquad pK_A = -\lg K_A$$

at 25 °C one finds: $$c(H^+) \cdot c(OH^-) = 10^{-14} \frac{mol^2}{L^2}$$

therefor: pH + pOH = 14

for neutral Water: pH = pOH = 7

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pK_A-values of some acid-base pairs at 25 C

increasing strenght of acid

Säure	Base	pK_s
$HClO_4$	ClO_4^-	-10
HCl	Cl^-	- 7
H_2SO_4	HSO_4^-	- 3,0
H_3O^+	H_2O	- 1,74
HNO_3	NO_3^-	- 1,37
HSO_4^-	SO_4^{2-}	+ 1,96
H_2SO_3	HSO_3^-	+ 1,90
H_3PO_4	$H_2PO_4^-$	+ 2,16
$[Fe(H_2O)_6]^{3+}$	$[Fe(OH)(H_2O)_5]^{2+}$	+ 2,46
HF	F^-	+ 3,18
CH_3COOH	CH_3COO^-	+ 4,75
$[Al(H_2O)_6]^{3+}$	$[Al(OH)(H_2O)_5]^{2+}$	+ 4,97
$CO_2 + H_2O$	HCO_3^-	+ 6,35
$[Fe(H_2O)_6]^{2+}$	$[Fe(H_2O)_5OH]^+$	+ 6,74
H_2S	HS^-	+ 6,99
HSO_3^-	SO_3^{2-}	+ 7,20
$H_2PO_4^-$	HPO_4^{2-}	+ 7,21
$[Zn(H_2O)_6]^{2+}$	$[Zn(H_2O)_5OH]^+$	+ 8,96
HCN	CN^-	+ 9,21
NH_4^+	NH_3	+ 9,25
HCO_3^-	CO_3^{2-}	+10,33
H_2O_2	HO_2^-	+11,65
HPO_4^{2-}	PO_4^{3-}	+12,32
HS^-	S^{2-}	+12,89
H_2O	OH^-	+15,74
OH^-	O^{2-}	+29

increasing strenght of base

Strong and weak acids and bases

Definition: Strong acids and bases dissociate completely

Definition: Weak acids and bases do not completely dissociate, but only (very) little.

For strong acids + bases, the calculation of pH or pOH is simple:

$$\text{pH} = \text{-lg}\, c_0(\text{HA}) \qquad \text{pOH} = \text{-lg}\, c_0(\text{BOH})$$

$$\text{for HA} \rightarrow \text{H}^+ + A^- \qquad \text{for BOH} \rightarrow \text{B}^+ + \text{OH}^-$$

A^- : acid residue B^+ : base residue

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pH calculation for weak acids

$$\text{for HA} \rightleftharpoons \text{H}^+ + A^- : \qquad K_A = \frac{c(\text{H}^+)c(\text{A}^-)}{c(\text{HA})}$$

2 simplifications:

1.: weak acids: (very) weak dissociated, therefore $c(\text{HA}) \approx c_0(\text{HA})$

2.: in spite of weak dissociation: $c(\text{H}^+)_{\text{water}} \ll c(\text{H}^+)_{\text{acid}}$

so we have $c(\text{H}^+) \approx c(\text{A}^-)$ and $K_A = \frac{c(\text{H}^+)c(\text{A}^-)}{c(\text{HA})} = \frac{c^2(\text{H}^+)}{c_0(\text{HA})}$

$$c^2(\text{H}^+) = K_A \cdot c_0(\text{HA}) \qquad c(\text{H}^+) = \sqrt{K_A \cdot c_0(\text{HA})}$$

logarithmic form: $\text{pH} = \frac{1}{2}\left(\text{pK}_\text{A} - \text{lg}\, c_0(\text{HA})\right)$

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How far do weak acids dissociate?

$$\text{for HA} \rightleftharpoons H^+ + A^-: \quad K_A = \frac{c(H^+)c(A^-)}{c(HA)}$$

Calculated for Acetic Acid and K_A = 1,8 ·10^-5^ mol L^-1^

$$c(H^+) = \sqrt{K_A \cdot c_0(HA)}$$

c_0 /mol L^{-1}	$c(H^+)$ /mol L^{-1}	pH
10^{-1}	$1,3\cdot10^{-3}$	2,9
10^{-3}	$1,3\cdot10^{-4}$	3,9
10^{-5}	$1,3\cdot10^{-5}$	4,9

Do the assumptions still apply here? →

For c_0 = 3,6 x 10^{-5} mol/l, we get 50% dissoziation

$$K_A = \frac{1,8\cdot10^{-5}\cdot1,8\cdot10^{-5}}{1,8\cdot10^{-5}} = 1,8\cdot10^{-5}\,\frac{\text{mol}}{\text{L}}$$

so pH = -lg(1,8 x 10^{-5}) = 4,74

Degree of dissociation α

$$\alpha = \frac{c(A^-)}{c_0(HA)} = \frac{c(H^+)}{c_0(HA)}$$

$$\alpha = \frac{\sqrt{K_A \cdot c_0(HA)}}{c_0(HA)} = \sqrt{\frac{K_A}{c_0(HA)}}$$

Calculation of buffer systems

$$K_A = \frac{c(\mathrm{H^+})c(\mathrm{A^-})}{c(\mathrm{HA})} \qquad = c(\mathrm{H^+})\frac{c(\mathrm{A^-})}{c(\mathrm{HA})}$$

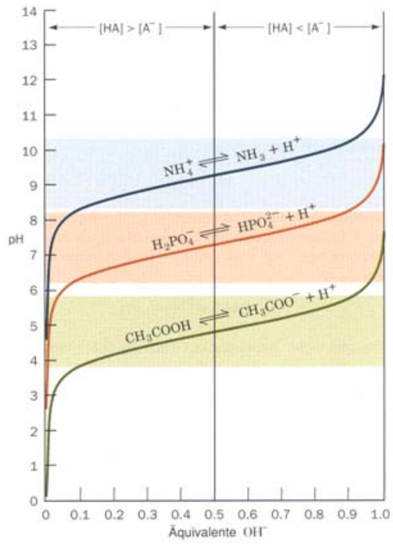
logarithmize, then multiply by -1:

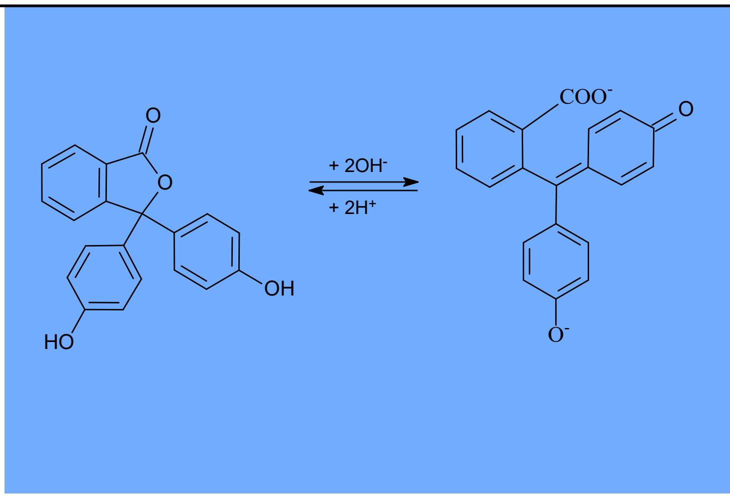
$$-\lg K_A = -\lg c(\mathrm{H^+}) - \lg\frac{c(\mathrm{A^-})}{c(\mathrm{HA})}$$

$$\mathrm{pK_A} = \mathrm{pH} - \lg\frac{c(\mathrm{A^-})}{c(\mathrm{HA})} \qquad \mathrm{pH} = \mathrm{pK}_A + \lg\frac{c(\mathrm{A^-})}{c(\mathrm{HA})}$$

$$\mathrm{pH} = \mathrm{pK}_A \text{ for } c(\mathrm{A^-}) = c(\mathrm{HA})$$

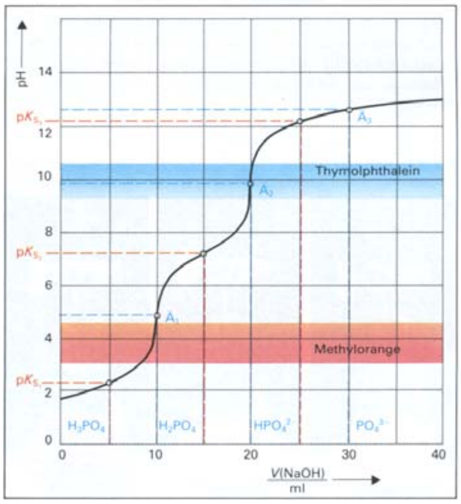
Buffered titration curves





„measuring pH"
Indicator molecule Phenolphthalein:
colorless in acidic and neutral solutions
pink in strong acidic solutions

Titration curve for H_3PO_4



$$AH_3 \rightleftharpoons H^+ + AH_2^-$$

$$AH_2^- \rightleftharpoons H^+ + AH^{2-}$$

$$AH^{2-} \rightleftharpoons H^+ + A^{3-}$$

Reactions in aqueous solutions

- Some essential terminology
- assigning oxidation states
- Balancing redox equations

Terminology

- Oxidation
- Reduction
- Redox-Reaction
- Oxidation Number

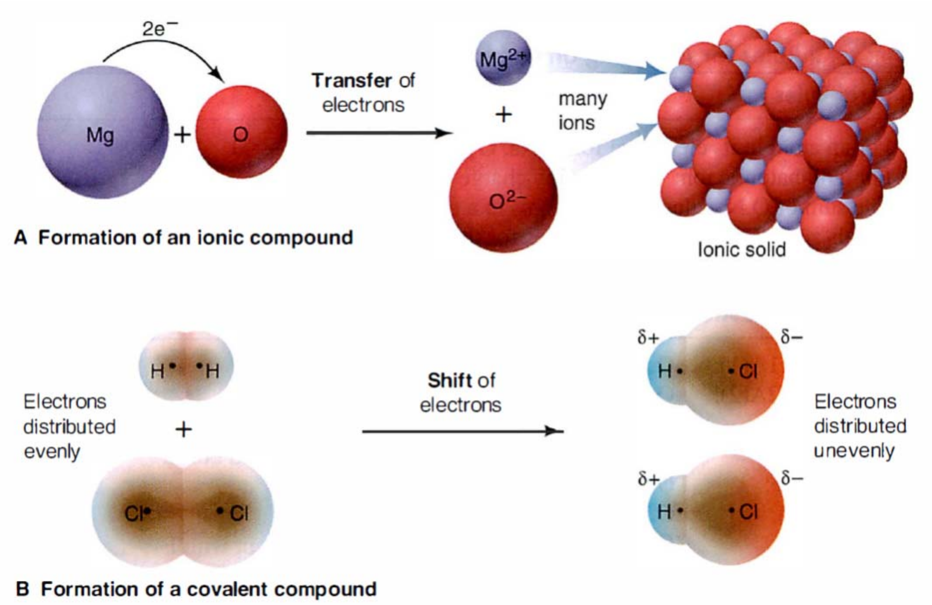


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Table 4.3 Rules for Assigning an Oxidation Number (O.N.)

General Rules

1. For an atom in its elemental form (Na, O_2, Cl_2, etc.): O.N. = 0
2. For a monatomic ion: O.N. = ion charge
3. The sum of O.N. values for the atoms in a molecule or formula unit of a compound equals zero. The sum of O.N. values for the atoms in a polyatomic ion equals the ion's charge.

Rules for Specific Atoms or Periodic Table Groups

1. For Group 1A(1):	O.N. = +1 in all compounds
2. For Group 2A(2):	O.N. = +2 in all compounds
3. For hydrogen:	O.N. = +1 in combination with nonmetals
	O.N. = −1 in combination with metals and boron
4. For fluorine:	O.N. = −1 in all compounds
5. For oxygen:	O.N. = −1 in peroxides
	O.N. = −2 in all other compounds (except with F)
6. For Group 7A(17):	O.N. = −1 in combination with metals, nonmetals (except O), and other halogens lower in the group

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Balancing Redox Equations

1. Write as much of the overall unbalanced equation as possible, omitting spectator ions.
2. Construct unbalanced oxidation and reduction half-reactions (these are usually incomplete as well as unbalanced). Show complete formulas for polyatomic ions and molecules.
3. Balance by inspection all elements in each half-reaction, except H and O. Then use the chart in Section 11-5 to balance H and O in each half-reaction.
4. Balance the charge in each half-reaction by adding electrons as "products" or "reactants."
5. Balance the electron transfer by multiplying the balanced half-reactions by appropriate integers.
6. Add the resulting half-reactions and eliminate any common terms.
7. Add common species that appear on the same side of the equation, and cancel equal amounts of common species that appear on opposite sides of the equation in equal amounts. The electrons must *always* cancel.
8. Check for mass balance (same number of atoms of each kind as reactants and products); check for charge balance (same total charge on both sides of the equation).

Example 11-10 Balancing Redox Equations

A useful analytical procedure involves the oxidation of iodide ions to free iodine. The free iodine is then titrated with a standard solution of sodium thiosulfate, $Na_2S_2O_3$. Iodine oxidizes $S_2O_3^{2-}$ ions to tetrathionate ions, $S_4O_6^{2-}$, and is reduced to I^- ions. Write the balanced net ionic equation for this reaction.

$$I_2 + S_2O_3^{2-} \longrightarrow I^- + S_4O_6^{2-}$$

$$I_2 \longrightarrow I^- \quad \text{(red. half-reaction)}$$

$$I_2 \longrightarrow 2I^-$$

$$I_2 + 2e^- \longrightarrow 2I^- \quad \text{(balanced red. half-reaction)}$$

$$S_2O_3^{2-} \longrightarrow S_4O_6^{2-} \quad \text{(ox. half-reaction)}$$

$$2S_2O_3^{2-} \longrightarrow S_4O_6^{2-}$$

$$2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2e^- \quad \text{(balanced ox. half-reaction)}$$

$$I_2 + 2e^- \longrightarrow 2I^-$$

$$2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2e^-$$

$$I_2(s) + 2S_2O_3^{2-}(aq) \longrightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$$

Balancing Oxygen and Hydrogen

In acidic solution: We add only H^+ or H_3O^+ (*not* OH^- in acidic solution).
In basic solution: We add only OH^- or H_2O (*not* H^+ in basic solution).

The following chart shows how to balance hydrogen and oxygen.

In *acidic* or *neutral* solution:

To balance O
For *each* O needed, add *one* H_2O

and ↓ then

To balance H
For *each* H needed, add *one* H^+

In *basic* solution:

To balance O
For *each* O needed, add *one* H_2O

and ↓ then

To balance H
For *each* H needed, add *one* H_2O to side needing H *and* add *one* OH^- to *other* side (This adds H without changing O)

Example 11-11 Balancing Net Ionic Equations (Acidic Solution)

Permanganate ions oxidize iron(II) to iron(III) in sulfuric acid solution. Permanganate ions are reduced to manganese(II) ions. Write the balanced net ionic equation for this reaction.

$$Fe^{2+} + MnO_4^- \longrightarrow Fe^{3+} + Mn^{2+}$$

$Fe^{2+} \longrightarrow Fe^{3+}$ (ox. half-reaction)

$Fe^{2+} \longrightarrow Fe^{3+} + 1e^-$ (balanced ox. half-reaction)

$MnO_4^- \longrightarrow Mn^{2+}$ (red. half-reaction)

$MnO_4^- + 8H^+ \longrightarrow Mn^{2+} + 4H_2O$

$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$ (balanced red. half-reaction)

$$5(Fe^{2+} \longrightarrow Fe^{3+} + 1e^-)$$
$$1(MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O)$$

$$5Fe^{2+}(aq) + MnO_4^-(aq) + 8H^+(aq) \longrightarrow 5Fe^{3+}(aq) + Mn^{2+}(aq) + 4H_2O(\ell)$$

Example 11-13 Balancing Redox Equations (Basic Solution)

In basic solution, hypochlorite ions, ClO^-, oxidize chromite ions, CrO_2^-, to chromate ions, CrO_4^{2-}, and are reduced to chloride ions. Write the balanced net ionic equation for this reaction.

$$CrO_2^- + ClO^- \longrightarrow CrO_4^{2-} + Cl^-$$

$$CrO_2^- \longrightarrow CrO_4^{2-} \qquad \text{(ox. half-rxn)}$$

$$CrO_2^- + 4OH^- \longrightarrow CrO_4^{2-} + 2H_2O$$

$$CrO_2^- + 4OH^- \longrightarrow CrO_4^{2-} + 2H_2O + 3e^- \qquad \text{(balanced ox. half-rxn)}$$

$$ClO^- \longrightarrow Cl^- \qquad \text{(red. half-rxn)}$$

$$ClO^- + H_2O \longrightarrow Cl^- + 2OH^-$$

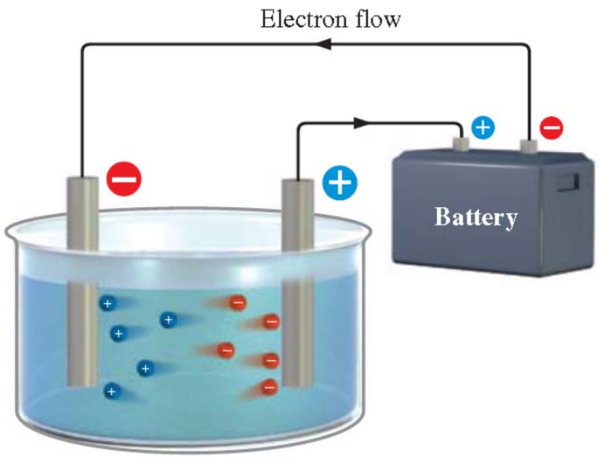
$$ClO^- + H_2O + 2e^- \longrightarrow Cl^- + 2OH^- \qquad \text{(balanced red. half-rxn)}$$

$$2(CrO_2^- + 4OH^- \longrightarrow CrO_4^{2-} + 2H_2O + 3e^-)$$

$$3(ClO^- + H_2O + 2e^- \longrightarrow Cl^- + 2OH^-)$$

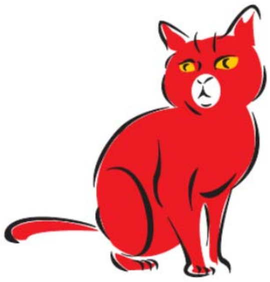
$$2CrO_2^- + 8OH^- + 3ClO^- + 3H_2O \longrightarrow 2CrO_4^{2-} + 4H_2O + 3Cl^- + 6OH^-$$

Electrochemistry

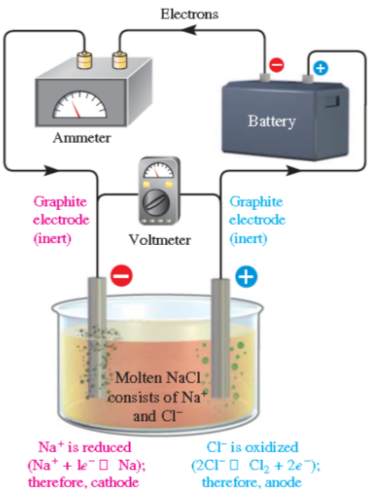


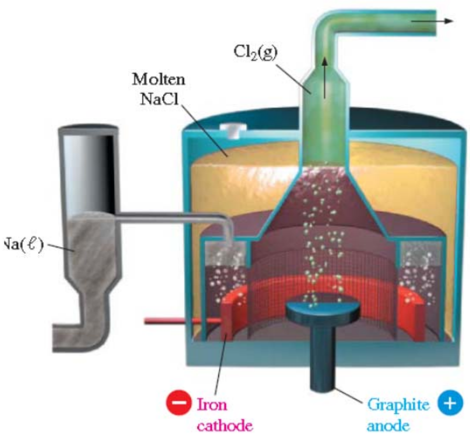
Electrodes

The **cathode** is defined as the electrode at which *reduction* occurs as electrons are gained by some species. The **anode** is the electrode at which *oxidation* occurs as electrons are lost by some species.

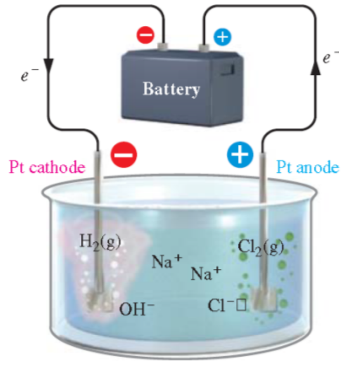


Electrolysis cells





Electrolysis cells



$$2Cl^- \longrightarrow Cl_2 + 2e^-$$ (oxidation, anode)

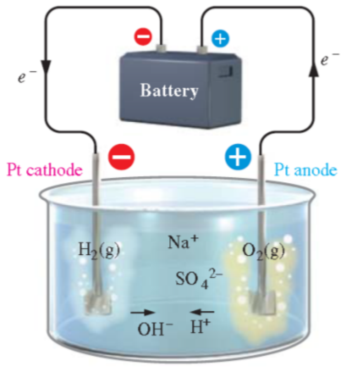
$$2H_2O + 2e^- \longrightarrow 2OH^- + H_2$$ (reduction, cathode)

$$2H_2O + 2Cl^- \longrightarrow 2OH^- + H_2 + Cl_2$$ (overall cell reaction as net ionic equation)

$$+ 2Na^+ \longrightarrow + 2Na^+$$ (spectator ions)

$$2H_2O + 2NaCl \longrightarrow 2NaOH + H_2 + Cl_2$$ (overall cell reaction as formula unit equation)

Electrolysis cells



$$2(2H_2O + 2e^- \longrightarrow H_2 + 2OH^-)$$ (reduction, cathode)

$$2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$$ (oxidation, anode)

$$6H_2O \longrightarrow 2H_2 + O_2 + \underbrace{4H^+ + 4OH^-}_{4H_2O}$$ (overall cell reaction)

$$2H_2O \longrightarrow 2H_2 + O_2$$ (net reaction)

Faraday's Law

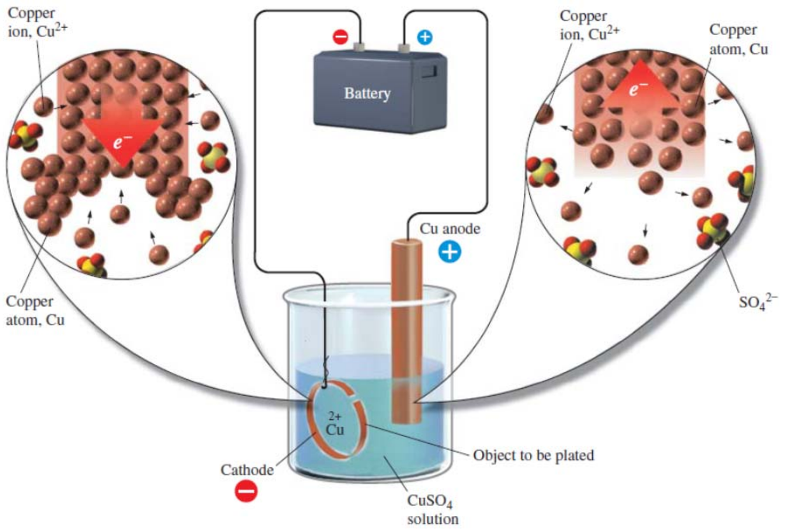
One **faraday** is the amount of electricity that corresponds to the gain or loss, and therefore the passage, of 6.022×10^{23} electrons, or *one mole* of electrons.

$$1 \text{ faraday} = 6.022 \times 10^{23}\ e^- = 96{,}485 \text{ C}$$

Table 21-1 Amounts of Elements Produced at One Electrode in Electrolysis by 1 Faraday of Electricity

Half-Reaction	Number of e^- in Half-Reaction	Product (electrode)	Amount Produced
$Ag^+(aq) + e^- \longrightarrow Ag(s)$	1	Ag (cathode)	1 mol = 107.868 g
$2H^+(aq) + 2e^- \longrightarrow H_2(g)$	2	H_2 (cathode)	$\frac{1}{2}$ mol = 1.008 g
$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$	2	Cu (cathode)	$\frac{1}{2}$ mol = 31.773 g
$Au^{3+}(aq) + 3e^- \longrightarrow Au(s)$	3	Au (cathode)	$\frac{1}{3}$ mol = 65.656 g
$2Cl^-(aq) \longrightarrow Cl_2(g) + 2e^-$	2	Cl_2 (anode)	$\frac{1}{2}$ mol = 35.453 g = 11.2 L_{STP}
$2H_2O(\ell) \longrightarrow O_2(g) + 4H^+(aq) + 4e^-$	4	O_2 (anode)	$\frac{1}{4}$ mol = 8.000 g = 5.60 L_{STP}

Electroplating with copper



Voltaic (or Galvanic) Cells:
The zinc-copper cell

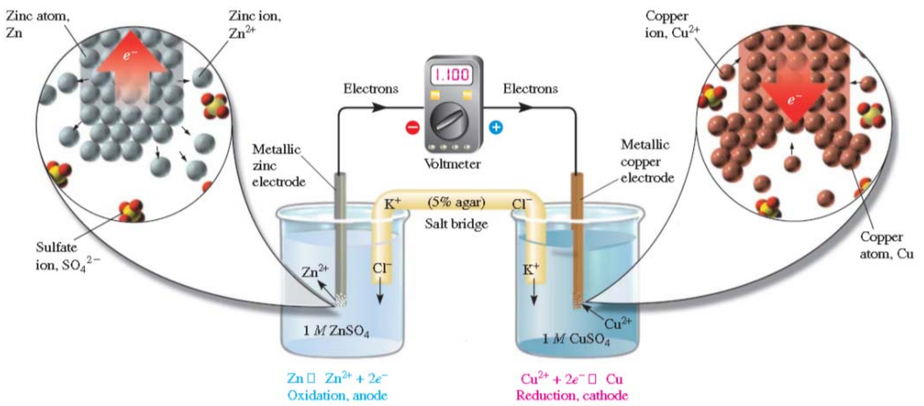


Figure 21-6 The zinc–copper voltaic cell utilizes the reaction

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