Conditional Formation Constant

- The formation constant **$K_f = [MY^{n-4}]/[M^{n+}][Y^{4-}]$**

  → describes the reaction between Y^{4-} and a metal ion (M^{n+}).
- (Figure 12-7) most EDTA is not Y^{4-} below pH 10.37.

  → The species HY^{3-}, H_2Y^{2-}, and so on, predominate at lower pH.
- From the definition **$\alpha_{Y4-} = [Y^{4-}]/[EDTA]$,**

  → we can express the concentration of Y^{4-} as

$$[Y^{4-}] = \alpha_{Y^{4-}}[\mathrm{EDTA}]$$

  → where [EDTA] is the total concentration of all EDTA species not bound to metal ion.
- The formation constant can now be rewritten as

$$K_f = \frac{[MY^{n-4}]}{[M^{n+}][Y^{4-}]} = \frac{[MY^{n-4}]}{[M^{n+}]\alpha_{Y^{4-}}[\mathrm{EDTA}]}$$

- If the pH is fixed by a buffer,

  → then α_{Y4-} is a constant that can be combined with K_f :

$$K_f = \frac{[MY^{n-4}]}{[M^{n+}][Y^{4-}]} = \frac{[MY^{n-4}]}{[M^{n+}]\alpha_{Y^{4-}}[EDTA]}$$

Conditional formation constant:

$$K_f' = \alpha_{Y^{4-}} K_f = \frac{[MY^{n-4}]}{[M^{n+}][EDTA]}$$

- The number $K_f' = \alpha_{Y4-}K_f$

  → called the **conditional formation constant** , or the effective formation constant.

- It describes the formation of MY^{n-4} at any particular pH.

EXAMPLE Using the Conditional Formation Constant

The formation constant in Table 12-2 for CaY^{2-} is $10^{10.65}$. Calculate the concentration of free Ca^{2+} in a solution of 0.10 M CaY^{2-} at pH 10.00 and at pH 6.00.

Solution The complex formation reaction is

$$Ca^{2+} + EDTA \rightleftharpoons CaY^{2-} \qquad K_f' = \alpha_{Y^{4-}} K_f$$

where EDTA on the left side of the equation refers to all forms of unbound EDTA (Y^{4-}, HY^{3-}, H_2Y^{2-}, H_3Y^-, and so on). Using $\alpha_{Y^{4-}}$ from Table 12-1, we find

$$\text{At pH 10.00:} \quad K_f' = (0.30)(10^{10.65}) = 1.3_4 \times 10^{10}$$

$$\text{At pH 6.00:} \quad K_f' = (1.8 \times 10^{-5})(10^{10.65}) = 8.0 \times 10^{5}$$

Dissociation of CaY^{2-} must produce equal quantities of Ca^{2+} and EDTA, so we can write

	Ca^{2+}	+ EDTA	$\rightleftharpoons$	CaY^{2-}
Initial concentration (M)	0	0		0.10
Final concentration (M)	x	x		$0.10 - x$

$$\frac{[CaY^{2-}]}{[Ca^{2+}][EDTA]} = \frac{0.10 - x}{x^2} = K_f' = 1.3_4 \times 10^{10} \quad \text{at pH 10.00}$$

$$= 8.0 \times 10^{5} \quad \text{at pH 6.00}$$

Solving for x (= $[Ca^{2+}]$ = [EDTA]), we find $[Ca^{2+}] = 2.7 \times 10^{-6}$ M at pH 10.00 and 3.5×10^{-4} M at pH 6.00. *Using the conditional formation constant at a fixed pH, we treat the dissociated EDTA as if it were a single species.*

TEST YOURSELF Find $[Ca^{2+}]$ in 0.10 M CaY^{2-} at pH 8.00 (*Answer:* 2.3×10^{-5} M)

- For a titration reaction to be effective,

  → it must go “to completion” (say, 99.9%),

  → means that the equilibrium constant is large

  → the analyte and titrant are essentially completely reacted at the equivalence point.

- You can see from the example that a metal-EDTA complex becomes less stable at lower pH.

12.3 EDTA Titration Curves

- In this section,

  → we calculate the concentration of free M^{n+} during its titration with EDTA.

- The titration reaction is.

$$M^{n+} + \text{EDTA} \rightleftharpoons MY^{n-4} \qquad K_f' = \alpha_{Y^{4-}} K_f$$

- If K_f' is large,

  → we can consider the reaction to be complete at each point in the titration.

- The titration curve

  → a graph of **pM (= – log[M^{n+}])** vs. **the volume of added EDTA** .

  → analogous to plotting pH vs. volume of titrant in an acid-base titration.

- There are three natural regions of the titration curve in Figure 12-11.

See Figure 12-11

Region 1: Before the Equivalence Point

- In this region,

  → there is excess M^{n+} left in solution after the EDTA has been consumed.

- The concentration of free metal ion

  → equal to the concentration of excess, unreacted M^{n+} .

- The dissociation of MY^{n-4} is negligible.

Region 2: At the Equivalence Point

- There is exactly as much EDTA as metal in the solution.

- We can treat the solution as if it had been made by dissolving pure MY^{n-4}.

- Some free M^{n+} is generated by the slight dissociation of MY^{n-4} :

$$\mathrm{MY}^{n-4} \rightleftharpoons \mathrm{M}^{n+} + \mathrm{EDTA}$$

→ In this reaction, EDTA represents free EDTA in all its forms.

→ At the equivalence point, $[M^{n+}] = [EDTA]$.

Region 3: After the Equivalence Point

- Now there is excess EDTA,

  → virtually all the metal ion is in the form MY^{n-4}.

- The concentration of free EDTA

  → can be equated to the concentration of excess EDTA added after the equivalence point.

Titration Calculations

- We want to make a graph of **pCa^{2+} (= $-\log[Ca^{2+}]$)** vs. **milliliters of added EDTA** .

- Let's calculate the shape of the titration curve for the reaction of 50.0 mL of 0.040 0 M Ca^{2+} (buffered to pH 10.00) with 0.080 0 M EDTA:

$$Ca^{2+} + \text{EDTA} \rightarrow CaY^{2-}$$

$$K_f' = \alpha_{Y^{4-}} K_f = (0.30)(10^{10.65}) = 1.3_4 \times 10^{10}$$

- Because K_f' is large,
  → it is reasonable to say that the reaction goes to completion with each addition of titrant.

- The equivalence volume is 25.0 mL.

Region 1: Before the Equivalence Point

- Before the equivalence point,

  → there is excess unreacted Ca^{2+}.
- Consider the addition of 5.0 mL of EDTA.
- Because the equivalence point requires 25.0 mL of EDTA,

  → one-fifth of the Ca^{2+} will be consumed and four-fifths remains.

$$[\mathrm{Ca}^{2+}] = \underbrace{\left(\frac{25.0-5.0}{25.0}\right)}_{\substack{\text{Fraction}\\ \text{remaining}\\ (=4/5)}} \underbrace{(0.040\,0\ \mathrm{M})}_{\substack{\text{Original}\\ \text{concentration}\\ \text{of Ca}^{2+}}} \underbrace{\left(\frac{\overset{\text{Initial volume of Ca}^{2+}}{50.0}}{\underset{\text{Total volume of solution}}{55.0}}\right)}_{\substack{\text{Dilution}\\ \text{factor}}}$$

$$= 0.029\,1\ \mathrm{M} \Rightarrow \mathrm{pCa}^{2+} = -\log[\mathrm{Ca}^{2+}] = 1.54$$

- In a similar manner,

  → we could calculate pCa^{2+} for any volume of EDTA less than 25.0 mL.

Region 2: At the Equivalence Point

- Virtually all the metal is in the form CaY^{2-}.
- Assuming no dissociation,

→ the concentration of CaY^{2-} is equal to the original concentration of Ca^{2+}, with a correction for dilution.

$$[\mathrm{CaY}^{2-}] = \underbrace{(0.040\,0\ \mathrm{M})}_{\substack{\text{Original}\\ \text{concentration}\\ \text{of Ca}^{2+}}} \underbrace{\left(\frac{\overset{\substack{\text{Initial volume}\\ \text{of Ca}^{2+}}}{50.0}}{\underset{\substack{\text{Total volume}\\ \text{of solution}}}{75.0}}\right)}_{\substack{\text{Dilution}\\ \text{factor}}} = 0.026\,7\ \mathrm{M}$$

- At the equivalence point,

  → the major species is CaY^{2-}, in equilibrium with small, equal amounts of free Ca^{2+} and EDTA.

- The concentration of free Ca^{2+} is calculated as:

	Ca^{2+}	$+$	EDTA	$\rightleftharpoons$	CaY^{2-}
Initial concentration (M)	—		—		0.026 7
Final concentration (M)	x		x		$0.026\,7 - x$

$$\frac{[CaY^{2-}]}{[Ca^{2+}][EDTA]} = K'_f = 1.3_4 \times 10^{10}$$

$$\frac{0.026\,7 - x}{x^2} = 1.3_4 \times 10^{10} \Rightarrow x = 1.4 \times 10^{-6}\ \text{M}$$

$$pCa^{2+} = -\log[Ca^{2+}] = -\log x = 5.85$$

Region 3: After the Equivalence Point

- In this region,

  → virtually all the metal is in the form CaY^{2-},

  → there is excess, unreacted EDTA.

- For example, at 26.0 mL, there is 1.0 mL of excess EDTA.

  → The concentrations of CaY^{2-} and excess EDTA are easily calculated.

$$[\text{EDTA}] = \underbrace{(0.080\,0\text{ M})}_{\substack{\text{Original}\\ \text{concentration}\\ \text{of EDTA}}} \underbrace{\left(\frac{\overset{\substack{\text{Volume of}\\ \text{excess EDTA}}}{1.0}}{\underset{\substack{\text{Total volume}\\ \text{of solution}}}{76.0}}\right)}_{\substack{\text{Dilution}\\ \text{factor}}} = 1.05 \times 10^{-3}\text{ M}$$

Original volume of Ca^{2+}

$$[\mathrm{CaY}^{2-}] = \underbrace{(0.040\,0\ \mathrm{M})}_{\substack{\text{Original}\\ \text{concentration}\\ \text{of Ca}^{2+}}} \underbrace{\left(\frac{50.0}{76.0}\right)}_{\substack{\text{Dilution}\\ \text{factor}}} = 2.63 \times 10^{-2}\ \mathrm{M}$$

Total volume of solution

- The concentration of Ca^{2+} is governed by

$$\frac{[\mathrm{CaY}^{2-}]}{[\mathrm{Ca}^{2+}][\mathrm{EDTA}]} = K_f' = 1.3_4 \times 10^{10}$$

$$\frac{[2.63 \times 10^{-2}]}{[\mathrm{Ca}^{2+}](1.05 \times 10^{-3})} = 1.3_4 \times 10^{10}$$

$$[\mathrm{Ca}^{2+}] = 1.9 \times 10^{-9}\ \mathrm{M} \Rightarrow \mathrm{pCa}^{2+} = 8.73$$

The Titration Curve

See Figure 12-12

End-point detection methods:

1. Metal ion indicators

2. Mercury electrode

3. Ion-selective electrode

4. Glass (pH) electrode

Analytical Chemistry

Chapter 14. Fundamentals of Electrochemistry
Chapter 15. Electrodes and Potentiometry

Introduction and Overview of Electrode Process

➔ the terms and concepts for describing electrochemical reactions

Electrochemical Cells and Reactions

Electrochemistry

The branch of chemistry

→ concerned with the interrelation of electrical and chemical effects.

Deals with the study of

→ chemical changes caused by the passage of an electric current

→ the production of electrical energy by chemical reactions.

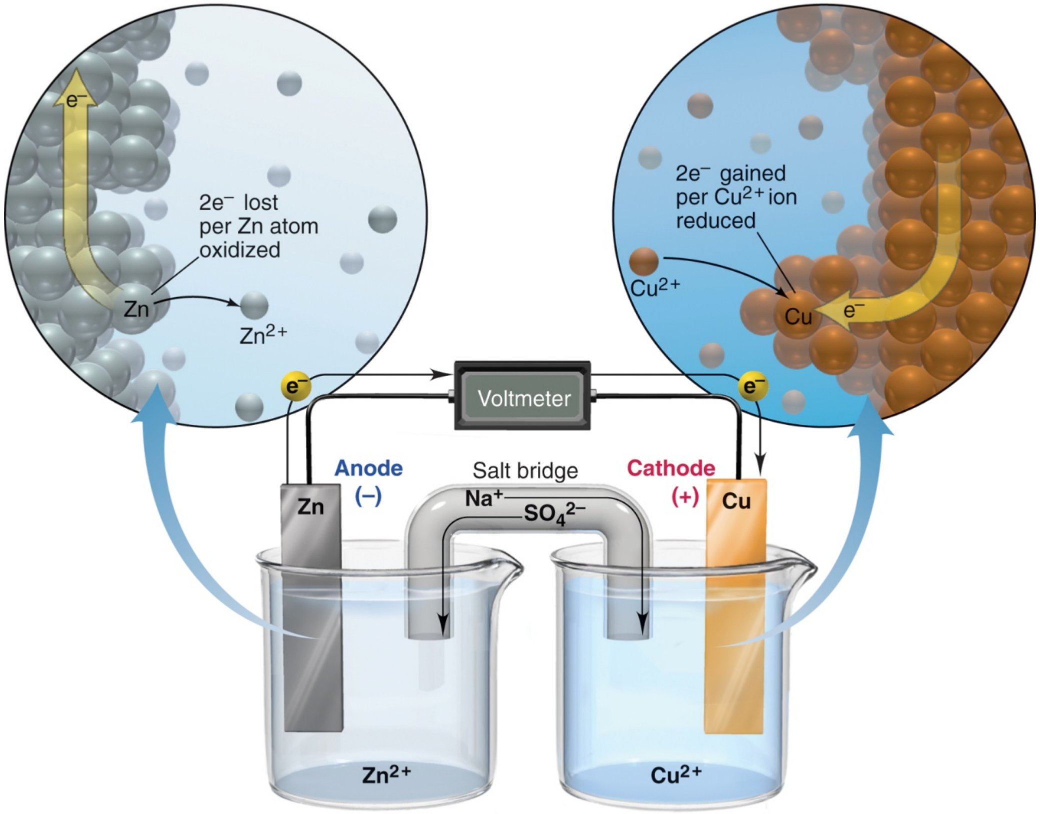
electrophoresis, corrosion, electrochromic displays, electro analytical sensors, batteries, fuel cells, and electroplating

Electrochemical Cells and Reactions

Generally defined as two electrodes separated by at least one electrolyte phase

A difference in electric potential (cell potential)

→ can be measured between the electrodes in an electrochemical cell



- Oxidation and Reduction

$$Cu^{2+} + Zn \rightarrow Cu + Zn^{2+}$$

Electrode

Electrode

Charge is transported through the electrode

→ by the movement of electrons (and holes).

Typical electrode materials include

→ solid metals (e.g., Pt, Au), liquid metals (Hg, amalgams), carbon (graphite), and semiconductors (indium-tin oxide, Si).

Two types of electrode

→ anode (~~negative electrode~~) and cathode (~~positive electrode~~)

$$O + ne^{-} \underset{\text{Oxidation}}{\overset{\text{Reduction}}{\rightleftharpoons}} R$$

Anode – electrode where oxidation (losing e^-) occurs

Cathode – electrode where reduction (accepting e^-) occurs

Electrolyte

Electrolyte

In the electrolyte phase,

→ charge is carried by the movement of ions.

To be useful in an electrochemical cell,

→ the electrolyte must have sufficiently low resistance

(i.e., sufficiently ionically conductive)

→ indicating that the movement of ions is sufficiently fast

The most common electrolytes

: liquid solutions containing ionic species, such as, H^+, Na^+, Cl^-, in either water or a nonaqueous solvent.

Electrochemical Cells—Types and Definitions

Two types of Electrochemical cells

1) Galvanic cell

- ➔ Reactions occur spontaneously at the electrodes when they are connected externally by a conductor
- ➔ These cells are often employed in converting chemical energy into electrical energy.
- ➔ Galvanic cells of commercial importance include primary batteries and fuel cells

2) Electrolytic cell

- ➔ Reactions are driven by the imposition of an external voltage greater than the open-circuit potential of the cell
- ➔ Electroplating, production of chlorine, charging process of rechargeable batteries

Electrochemical cell

Cell potential

→ a measure of the energy available to drive charge externally between the electrodes

Measured in volts (V),

→ where 1 V = 1 joule/coulomb (J/C)

→ unit of charge: coulombs (C), where 1 C = 6.24 X 10^{18} electrons

1 V

→ produce 1 J when 1 C of electrons pass through the external circuit

Current, i

: the rate of flow of coulombs (or electrons)

: unit of a current = ampere (A)

: 1 A = 1 C/s.

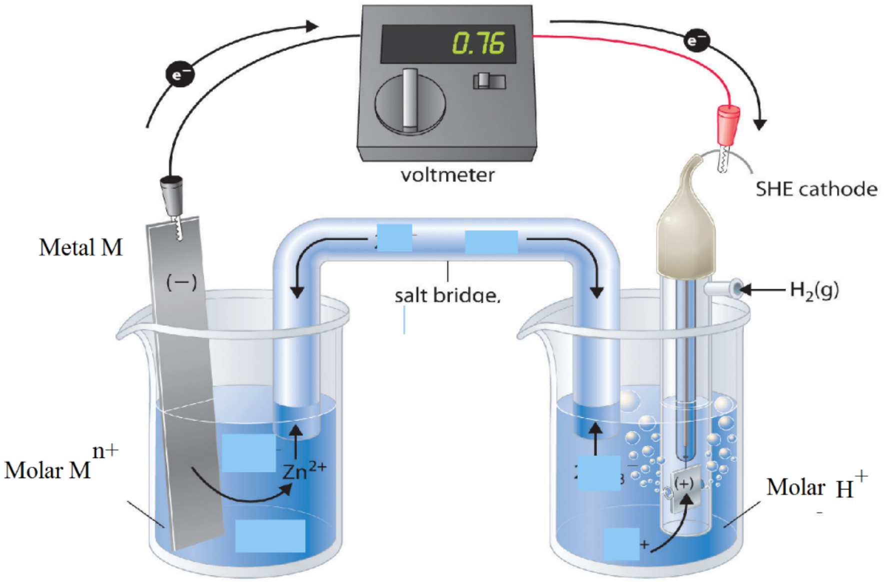
Number of electrons

The number of electrons that cross an interface

: stoichiometrically proportional to the extent of the chemical reaction

(i.e., to the amounts of reactant consumed and product generated).

$$O + ne^- \underset{\text{Oxidation}}{\overset{\text{Reduction}}{\rightleftarrows}} R$$



Number of electrons

The number of electrons is measured in terms of the total charge, Q, passed in the circuit.

The magnitude of the charge of a single electron

: 1.602×10^{-19} C

A mole of electrons = a charge of $(1.602 \times 10^{-19}\ \text{C})(6.022 \times 10^{23}\ \text{mol}^{-1}) = 9.649 \times 10^{4}$ C

: called the Faraday constant, F.

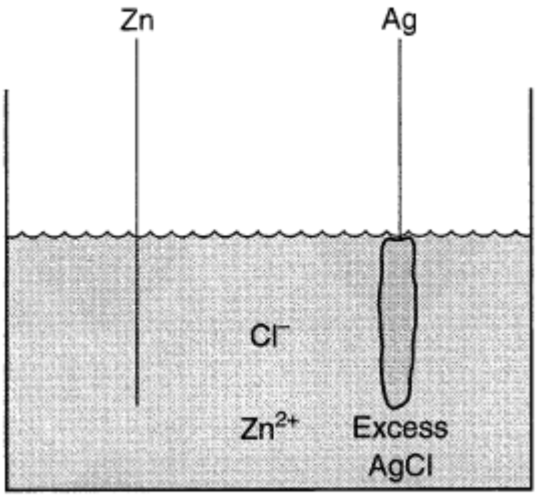
Faraday's law

: relationship between charge and amount of product formed

: the passage of 96,485.4 C → 1 mole of reaction for a one-electron reaction.

Electrochemical cell

A shorthand notation for expressing the structure of electrochemical cells



$$Zn/Zn^{2+}, Cl^{-}/AgCl/Ag$$

→ Slash: represents a phase boundary

→ Comma: separates two components in the same phase.

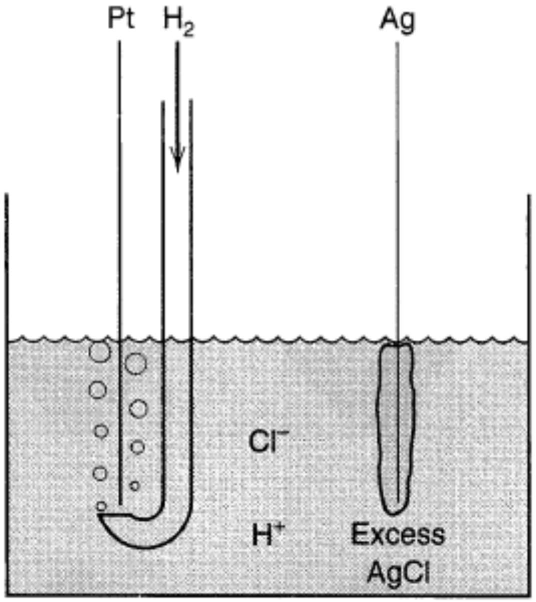
→ Double slash

: represents a phase boundary whose potential is regarded as a negligible component of the overall cell potential.

Electrochemical cell

When a gaseous phase is involved,

→ it is written adjacent to its corresponding conducting element.



$\underline{Pt/H_2}/H^+, Cl^-/AgCl/Ag$

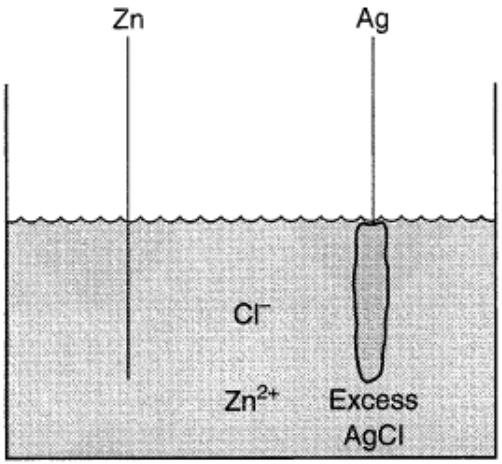
Electrochemical cell

The overall chemical reaction taking place in a cell is made up of two independent half-reactions

→ Describe the real chemical changes at the two electrodes.

Each half reaction (and, consequently, the chemical composition of the system near the electrodes)

→ responds to the interfacial potential difference at the corresponding electrode.



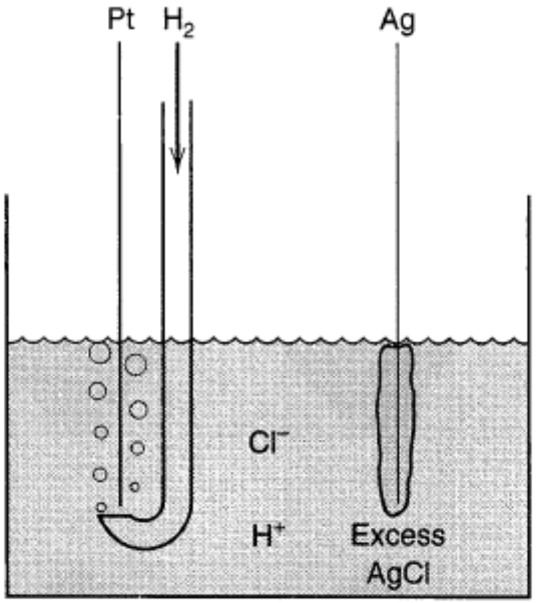
$Zn/Zn^{2+}, Cl^{-}/AgCl/Ag$

Anode half-reaction: $Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$

Cathode half-reaction: $2AgCl(s) + 2e^- \longrightarrow 2Ag(s) + 2Cl^-(aq)$

Overall cell reaction: $Zn(s) + 2AgCl(s) \longrightarrow Zn^{2+}(aq) + 2Ag(s) + 2Cl^-(aq)$

Electrochemical cell



$Pt/H_2/H^+, Cl^-/AgCl/Ag$

Anode half-reaction: $H_2(g) \longrightarrow 2H^+(aq) + 2e^-$

Cathode half-reaction: $2AgCl(s) + 2e^- \longrightarrow 2Ag(s) + 2Cl^-(aq)$

Overall cell reaction: $H_2(g) + 2AgCl(s) \longrightarrow 2H^+(aq) + 2Ag(s) + 2Cl^-(aq)$

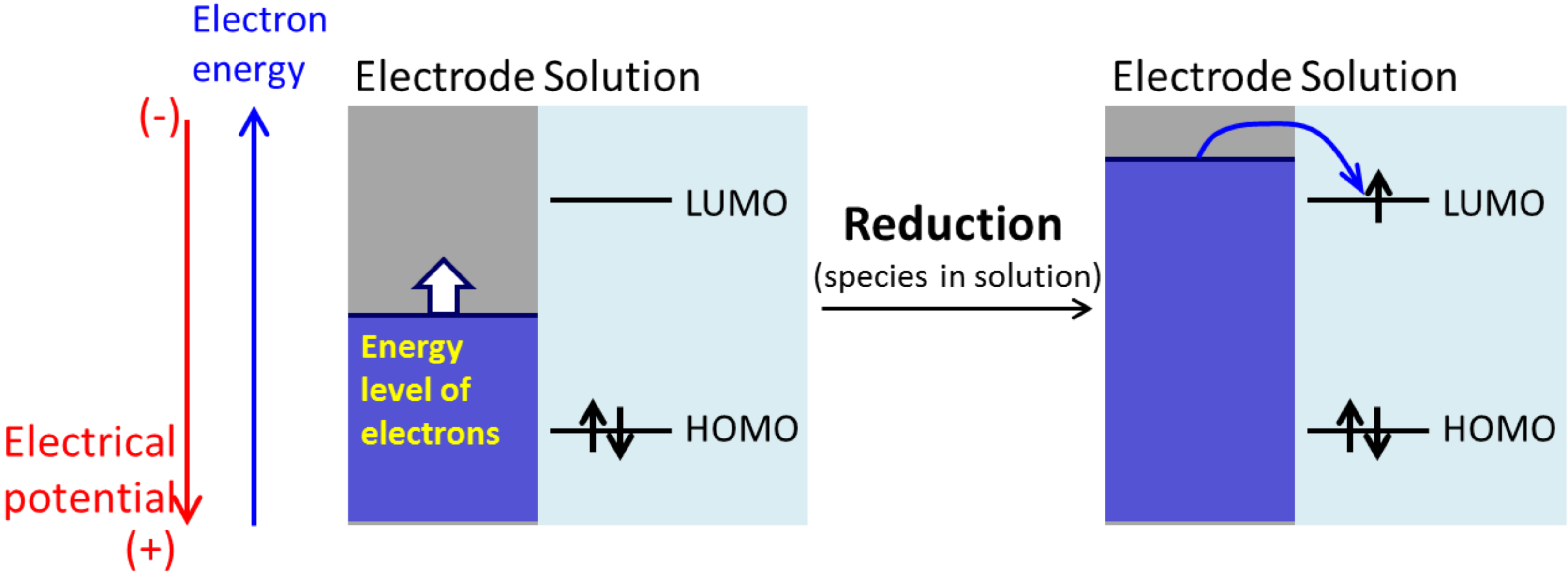
Charge transport: reduction

By driving the electrode to more negative potentials using a power supply

→ The energy of the electrons is raised

→ They can reach a level high enough to transfer into vacant electronic states on species in the electrolyte

→ In that case, a flow of electrons from electrode to solution (a reduction current) occurs



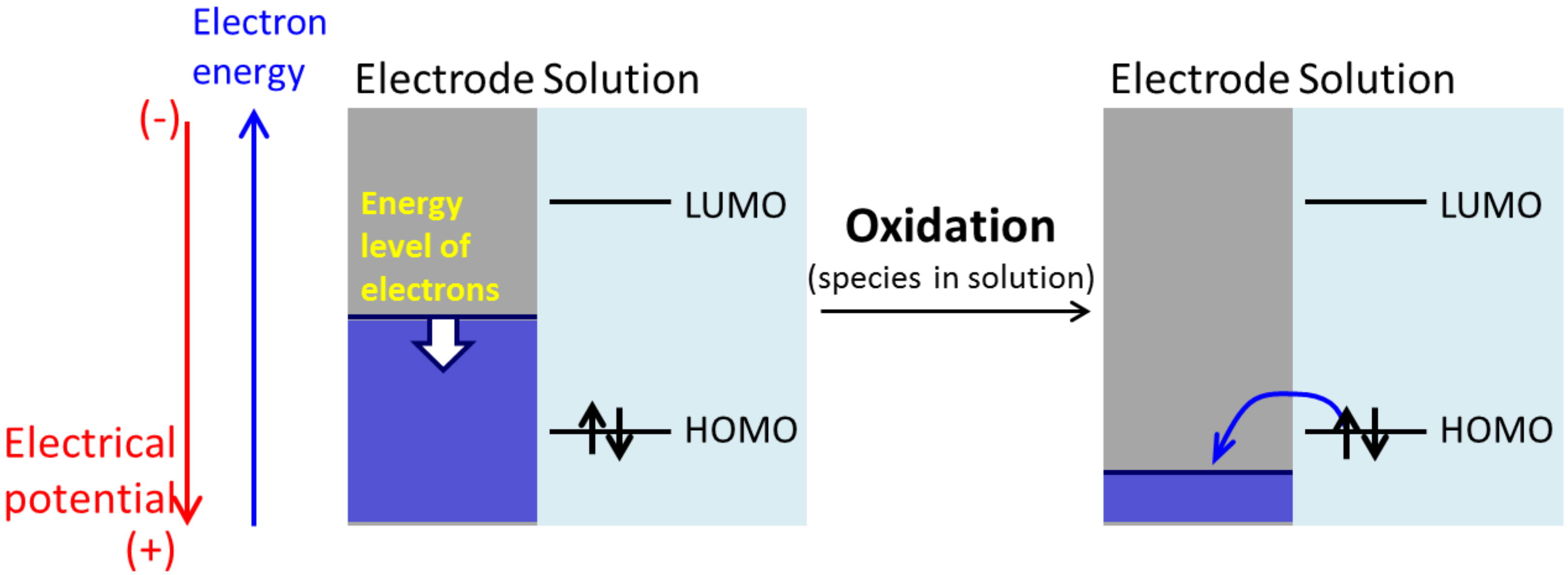
$$A + e \rightarrow A^{-}$$

Charge transport: oxidation

Similarly, the energy of the electrons can be lowered by imposing a more positive potential

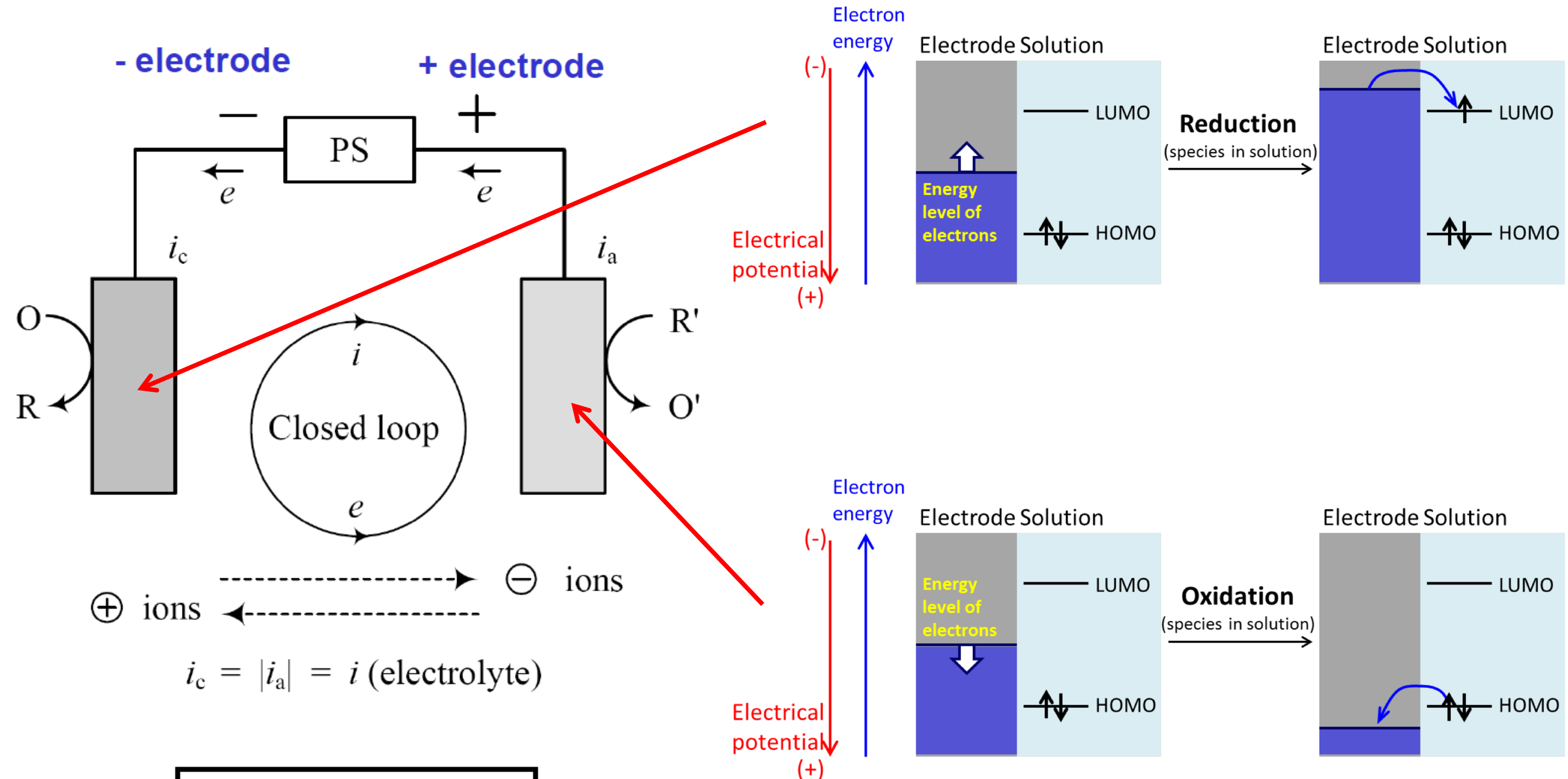
→ at some point, electrons on solutes in the electrolyte will transfer to a more stable energy on the electrode.

→ The electron flow from solution to electrode: oxidation current



$$\mathrm{A} - e \rightarrow \mathrm{A}^{+}$$

Current passes through “closed loop”



$$i_c = |i_a| = i\ (\text{electrolyte})$$

i_c: cathodic current

i_a : anodic current

Standard electrode potentials

The critical potentials at which these processes occur

→ related to the standard potentials, E°, for the specific chemical substances in the system.

→ Potentials at standard states (1M, 25°C)

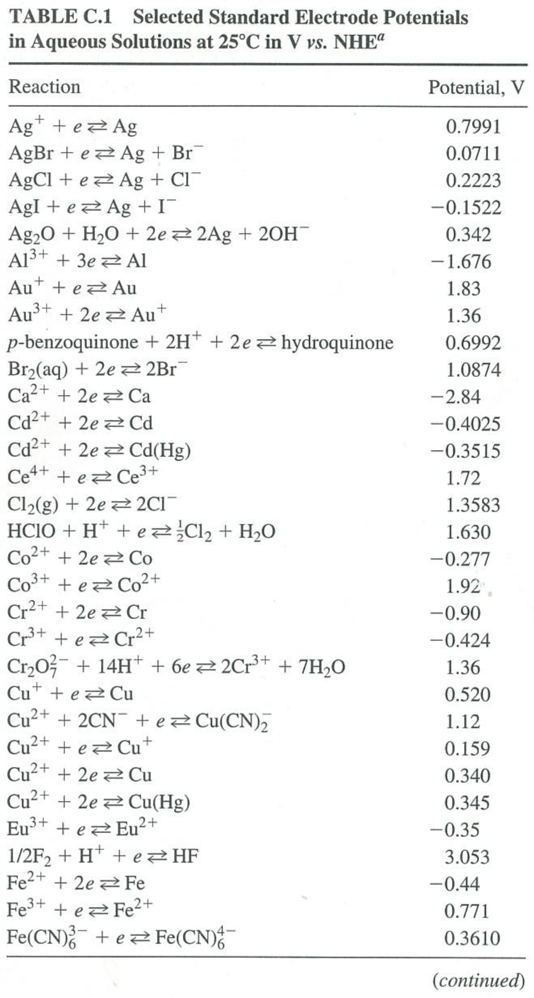


TABLE C.1 Selected Standard Electrode Potentials in Aqueous Solutions at 25°C in V *vs.* NHE[a]

Reaction	Potential, V
$Ag^+ + e \rightleftarrows Ag$	0.7991
$AgBr + e \rightleftarrows Ag + Br^-$	0.0711
$AgCl + e \rightleftarrows Ag + Cl^-$	0.2223
$AgI + e \rightleftarrows Ag + I^-$	−0.1522
$Ag_2O + H_2O + 2e \rightleftarrows 2Ag + 2OH^-$	0.342
$Al^{3+} + 3e \rightleftarrows Al$	−1.676
$Au^+ + e \rightleftarrows Au$	1.83
$Au^{3+} + 2e \rightleftarrows Au^+$	1.36
p-benzoquinone + $2H^+ + 2e \rightleftarrows$ hydroquinone	0.6992
$Br_2(aq) + 2e \rightleftarrows 2Br^-$	1.0874
$Ca^{2+} + 2e \rightleftarrows Ca$	−2.84
$Cd^{2+} + 2e \rightleftarrows Cd$	−0.4025
$Cd^{2+} + 2e \rightleftarrows Cd(Hg)$	−0.3515
$Ce^{4+} + e \rightleftarrows Ce^{3+}$	1.72
$Cl_2(g) + 2e \rightleftarrows 2Cl^-$	1.3583
$HClO + H^+ + e \rightleftarrows \frac{1}{2}Cl_2 + H_2O$	1.630
$Co^{2+} + 2e \rightleftarrows Co$	−0.277
$Co^{3+} + e \rightleftarrows Co^{2+}$	1.92
$Cr^{2+} + 2e \rightleftarrows Cr$	−0.90
$Cr^{3+} + e \rightleftarrows Cr^{2+}$	−0.424
$Cr_2O_7^{2-} + 14H^+ + 6e \rightleftarrows 2Cr^{3+} + 7H_2O$	1.36
$Cu^+ + e \rightleftarrows Cu$	0.520
$Cu^{2+} + 2CN^- + e \rightleftarrows Cu(CN)_2^-$	1.12
$Cu^{2+} + e \rightleftarrows Cu^+$	0.159
$Cu^{2+} + 2e \rightleftarrows Cu$	0.340
$Cu^{2+} + 2e \rightleftarrows Cu(Hg)$	0.345
$Eu^{3+} + e \rightleftarrows Eu^{2+}$	−0.35
$1/2F_2 + H^+ + e \rightleftarrows HF$	3.053
$Fe^{2+} + 2e \rightleftarrows Fe$	−0.44
$Fe^{3+} + e \rightleftarrows Fe^{2+}$	0.771
$Fe(CN)_6^{3-} + e \rightleftarrows Fe(CN)_6^{4-}$	0.3610

(continued)

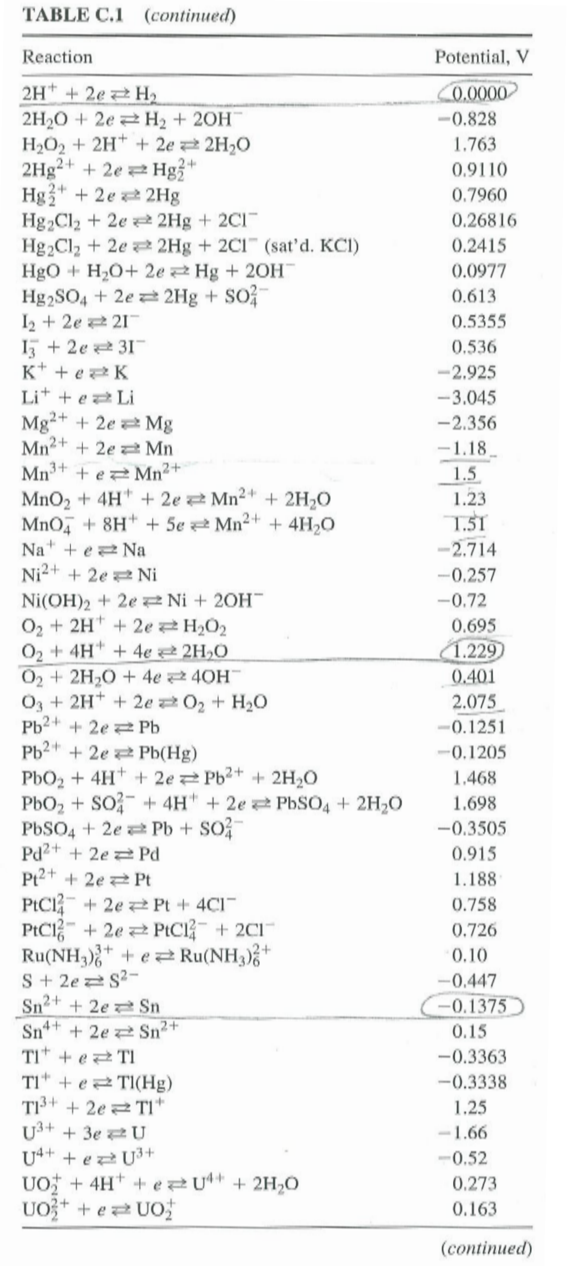


TABLE C.1 *(continued)*

Reaction	Potential, V
$2H^+ + 2e \rightleftarrows H_2$	0.0000
$2H_2O + 2e \rightleftarrows H_2 + 2OH^-$	−0.828
$H_2O_2 + 2H^+ + 2e \rightleftarrows 2H_2O$	1.763
$2Hg^{2+} + 2e \rightleftarrows Hg_2^{2+}$	0.9110
$Hg_2^{2+} + 2e \rightleftarrows 2Hg$	0.7960
$Hg_2Cl_2 + 2e \rightleftarrows 2Hg + 2Cl^-$	0.26816
$Hg_2Cl_2 + 2e \rightleftarrows 2Hg + 2Cl^-$ (sat'd. KCl)	0.2415
$HgO + H_2O + 2e \rightleftarrows Hg + 2OH^-$	0.0977
$Hg_2SO_4 + 2e \rightleftarrows 2Hg + SO_4^{2-}$	0.613
$I_2 + 2e \rightleftarrows 2I^-$	0.5355
$I_3^- + 2e \rightleftarrows 3I^-$	0.536
$K^+ + e \rightleftarrows K$	−2.925
$Li^+ + e \rightleftarrows Li$	−3.045
$Mg^{2+} + 2e \rightleftarrows Mg$	−2.356
$Mn^{2+} + 2e \rightleftarrows Mn$	−1.18
$Mn^{3+} + e \rightleftarrows Mn^{2+}$	1.5
$MnO_2 + 4H^+ + 2e \rightleftarrows Mn^{2+} + 2H_2O$	1.23
$MnO_4^- + 8H^+ + 5e \rightleftarrows Mn^{2+} + 4H_2O$	1.51
$Na^+ + e \rightleftarrows Na$	−2.714
$Ni^{2+} + 2e \rightleftarrows Ni$	−0.257
$Ni(OH)_2 + 2e \rightleftarrows Ni + 2OH^-$	−0.72
$O_2 + 2H^+ + 2e \rightleftarrows H_2O_2$	0.695
$O_2 + 4H^+ + 4e \rightleftarrows 2H_2O$	1.229
$O_2 + 2H_2O + 4e \rightleftarrows 4OH^-$	0.401
$O_3 + 2H^+ + 2e \rightleftarrows O_2 + H_2O$	2.075
$Pb^{2+} + 2e \rightleftarrows Pb$	−0.1251
$Pb^{2+} + 2e \rightleftarrows Pb(Hg)$	−0.1205
$PbO_2 + 4H^+ + 2e \rightleftarrows Pb^{2+} + 2H_2O$	1.468
$PbO_2 + SO_4^{2-} + 4H^+ + 2e \rightleftarrows PbSO_4 + 2H_2O$	1.698
$PbSO_4 + 2e \rightleftarrows Pb + SO_4^{2-}$	−0.3505
$Pd^{2+} + 2e \rightleftarrows Pd$	0.915
$Pt^{2+} + 2e \rightleftarrows Pt$	1.188
$PtCl_4^{2-} + 2e \rightleftarrows Pt + 4Cl^-$	0.758
$PtCl_6^{2-} + 2e \rightleftarrows PtCl_4^{2-} + 2Cl^-$	0.726
$Ru(NH_3)_6^{3+} + e \rightleftarrows Ru(NH_3)_6^{2+}$	0.10
$S + 2e \rightleftarrows S^{2-}$	−0.447
$Sn^{2+} + 2e \rightleftarrows Sn$	−0.1375
$Sn^{4+} + 2e \rightleftarrows Sn^{2+}$	0.15
$Tl^+ + e \rightleftarrows Tl$	−0.3363
$Tl^+ + e \rightleftarrows Tl(Hg)$	−0.3338
$Tl^{3+} + 2e \rightleftarrows Tl^+$	1.25
$U^{3+} + 3e \rightleftarrows U$	−1.66
$U^{4+} + e \rightleftarrows U^{3+}$	−0.52
$UO_2^+ + 4H^+ + e \rightleftarrows U^{4+} + 2H_2O$	0.273
$UO_2^{2+} + e \rightleftarrows UO_2^+$	0.163

(continued)