Chapter 20

Electrochemistry

Electrochemical Cell

Consists of electrodes which dip into an electrolyte & in which a chem. rxn. uses or generates an electric current

Voltaic (Galvanic) Cell

Spont. rxn. - produces electrical energy

- current supplied to external circuit

Electrolytic Cell

electrical energy is used to drive an otherwise nonspont. rxn.

I) Oxidation - Reduction Rx's (Redox)

Involves loss of e^- by one element &
gain of e^- by another element

Oxidation: lose e^-

(inc. in oxidation #)

Reduction: gain e^-

(dec. in oxidation #)

Oxidizing agent: substance that
(oxidant) is reduced

Reducing agent: substance that
(reductant) is oxidized

$$Zn + Br_2 \longrightarrow ZnBr_2$$

$$Zn \longrightarrow Zn^{2+} + 2\,e^-$$

Zn lost e^- $\Rightarrow$ oxidized

$$Br_2 + 2\,e^- \longrightarrow 2\,Br^-$$

Br gained e^- $\Rightarrow$ reduced

A) Oxidation Numbers

"Charge" an atom would have if both e^- in each bond are assigned to the more electronegative atom.

1) Elemental Form

Cu, H_2, O_2, S_8

ox. # = 0 (zero)

2) Monatomic Ion

ox. # = charge

Na^+, Zn^{2+}, Al^{3+}, O^{2-}, Br^-

Group IA ⇒ + 1 (Always)

Group IIA ⇒ + 2 (Always)

Group IIIA ⇒ + 3 (usually)

3) Hydrogen

H ⇒ +1 (usually)

exceptions

hydrides, H ⇒ −1

NaH , CaH_2

4) Oxygen

O ⇒ −2 (usually)

exceptions

peroxides, O_2^{2-} O ⇒ −1

H_2O_2 Na_2O_2

superoxides, O_2^{1-} O ⇒ −1/2

KO_2

5) Fluorine

F $\Rightarrow$ -1 Always

6) Halogens: Cl, Br, I

-1 except when combined w. a more E.N. element

CBr_4 : Br $\Rightarrow$ -1

can be : -1, 0, $+1$, $+3$, $+5$, $+7$

ClO_4^- : $+7$

7) Sum of ox. no.’s of atoms in neutral cmpds. =

0 (zero)

8) Sum of ox. no.’s of atoms in a polyatomic ion =

charge

9) Ox. no. can not be:

more positive than the group #

or

more negative than (group # − 8)

B) Examples

1) Ex 1: What is ox. # of N in NH_3 ?

$$\# \; x_N + 3(+1) = 0$$

$$\# \; x_N = -3$$

2) Ex 2: What is ox. # of N in NO_3^- ?

$$\# \; x_N + 3(-2) = -1$$

$$\# \; x_N = +5$$

3) Ex 3: What is ox. # of N in NO_2^- ?

$$\# \; x_N + 2(-2) = -1$$

$$\# \; x_N = +3$$

C) Redox Reactions

Involves transfer of e^- between species or change in ox. # of atoms

Oxidation: inc. in ox. #
(lose e^-)

Reduction: dec. in ox. #
(gain e^-)

1) Ex 1: Combustion

$$CH_4 + 2\,O_2 \longrightarrow CO_2 + 2\,H_2O$$

2) Ex 2: What is being oxidized and reduced? What is the oxidizing agent and reducing agent? How many electrons are transferred?

$$P_4 + 10\ HClO + H_2O \longrightarrow 4\ H_3PO_4 + 10\ HCl$$

III) Voltaic (Galvanic) Cells

Consists of 2 half-cells connected by an external circuit.

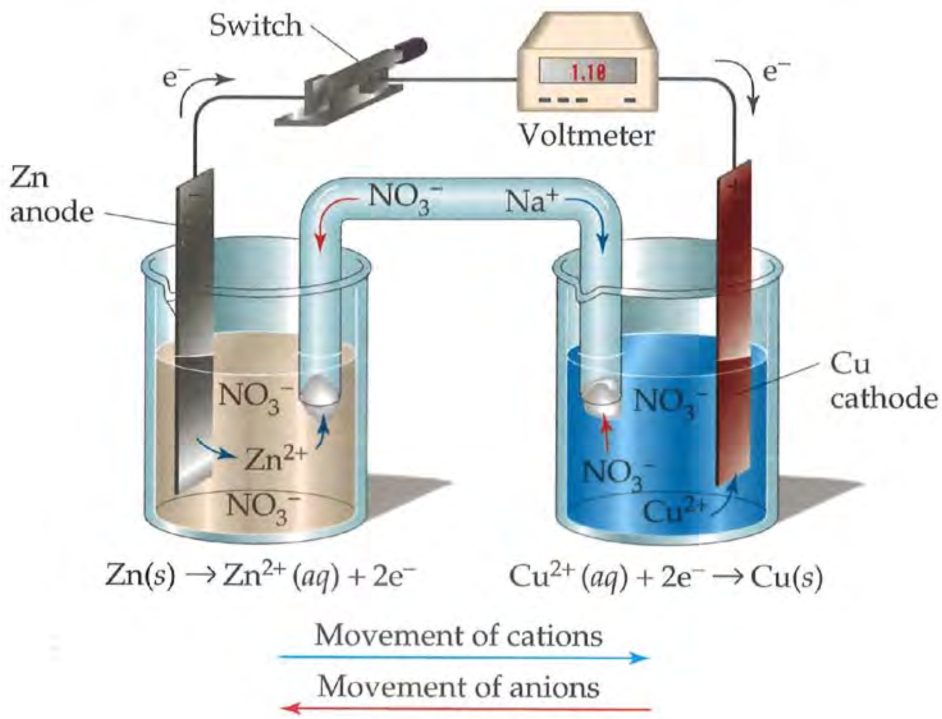
Half-cell

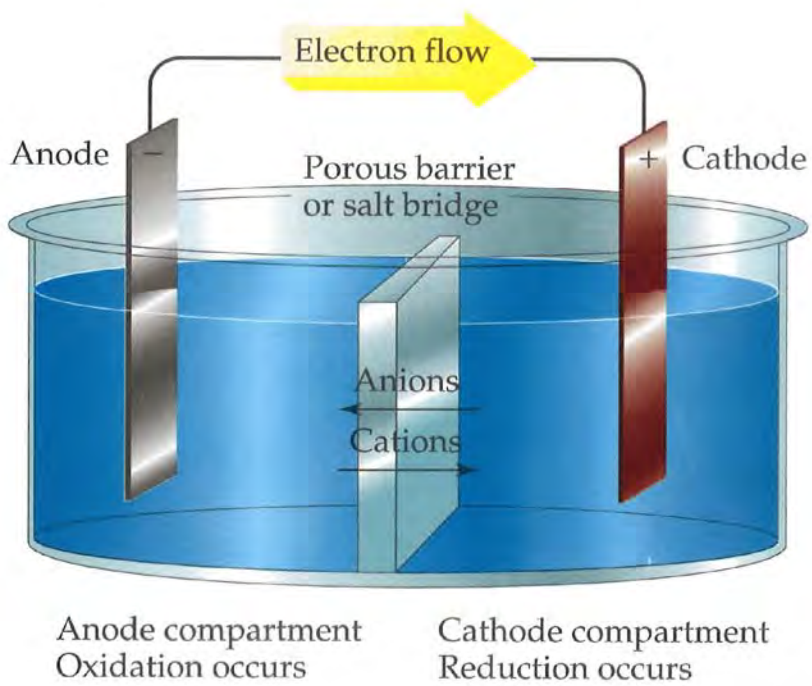
portion of an electrochem. cell in which a ½-rx occurs

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

Cell rxn : net rxn. which occurs in the voltaic cell

Fig. 20.5 Voltaic Cell
Fig. 20.6 Terminology Used in Describing Voltaic Cell





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A) Half-cell Rxns

1) Anode (−)

Anode : electrode at which ox. occurs

ox. half-rx

$$Zn\,(s) \longrightarrow Zn^{2+}\,(aq) + 2\,e^{-}$$

Zn^{2+} ions produced at electrode

- move away leaving e^{-} behind

e^{-} flow out of anode

(towards the cathode)

2) Cathode (+)

Cathode : electrode at which
red. occurs

red. half-rx

$$Cu^{2+}\,(aq) + 2\,e^{-} \longrightarrow Cu\,(s)$$

Cu^{2+} ions discharged at electrode

- removes e^{-} from electrode

e^{-} flow into the cathode

(appears to attract e^{-})

Soln. on right has a − chg.

Soln. on left has a + chg.

anions must move from

lt. ⟵ rt.

Accomplishes 2 things

1) Carry chg.

2) Preserves electrical neutrality

Salt Bridge

tube of electrolyte in a gel
connected to the half-cells

- allows flow of ions but prevents mixing of the diff. solns.

B) Cell Notation

Shorthand description of cell

1) Ions in soln.

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

anode salt bridge cathode

| vertical line is a phase boundary

begin & end w. electrodes

anode :

cathode :

2) Gaseous Reactant or Product

use inert electrode

$Zn(s)\ |\ Zn^{2+}(aq)\ \|\ Cl_2(g)\ |\ Cl^{-}(aq)\ |\ Pt(s)$

anode salt bridge cathode

anode :

cathode :

3) Ions in Diff. Ox. States

use inert electrode

$Sn(s) \mid Sn^{2+}(aq) \parallel Sn^{4+}(aq), Sn^{2+}(aq) \mid Pt$

anode — salt bridge — cathode

anode :

cathode :

IV) Standard Cell (Electrode) Potentials

A) Electromotive Force

Work req. to move a charge from a region of low electric pot. energy to a region of high electric pot. energy.

$$w \quad = \quad \text{charge} \times \Delta\text{P.E.}$$

Joules = Coulombs • Volts

1 J = 1 C • V

ΔP.E. (V) : diff. in electric potential between 2 points work done by a voltaic cell to move n moles of e^- is given by:

$$w_{max} = -nFE_{cell}$$

F : faraday constant, 9.65×10^4 C

charge on 1 mole of e^-

E_{cell} : electromotive force (emf)

max. potential diff. between electrodes of a cell

$$\Delta G = -nFE_{cell}$$

NOTE : Spont. rxn.

$\Delta G < 0$ $E_{cell} > 0$

B) Cell (Electrode) Potentials

$$E_{cell} = E_{red} + E_{ox}$$

$$E_{ox} = -E_{red} \text{ for reverse rxn.}$$

Tabulate reduction pot.
called electrode pot., E_{red}

$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^- \quad E_{ox} = -E_{Zn}$$

$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s) \quad E_{red} = E_{Cu}$$

$$E_{cell} = E_{Cu} + (-E_{Zn})$$

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

$$\boxed{E_{cell} = E_{cathode} - E_{anode}}$$

C) Standard Reduction Potentials

Standard emf : E^{o}_{cell}

emf of a cell under standard-state conditions

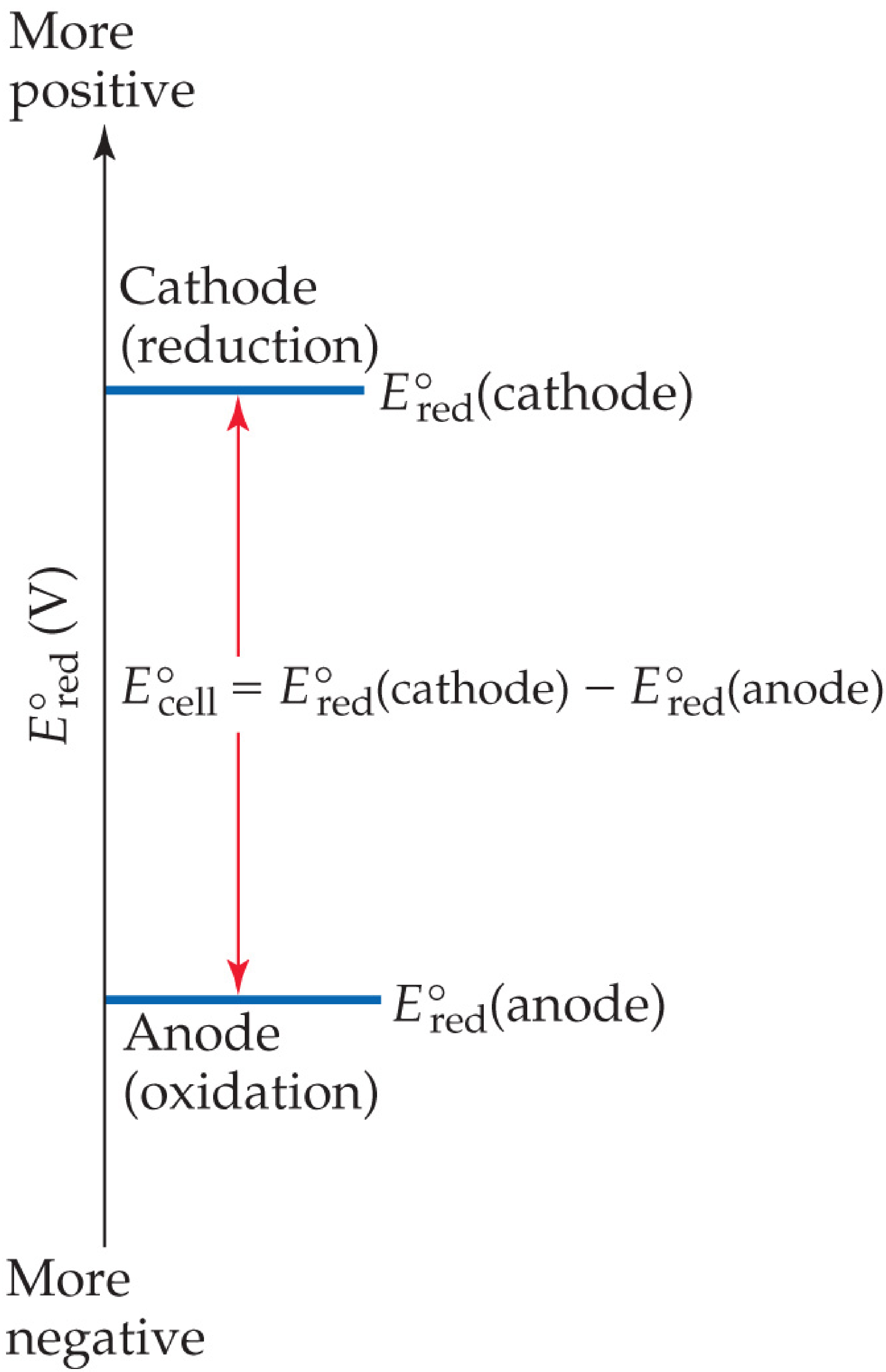
Standard reduction pot. E^{o}_{red}

reduction (electrode) pot. when conc. of solutes are 1 M & gas pressures are 1 atm, at a specified temp.

- measured relative to a reference electrode
  - standard H electrode (SHE)

$$2\,H^{+}\,(aq) + 2\,e^{-} \longrightarrow H_2\,(g)$$

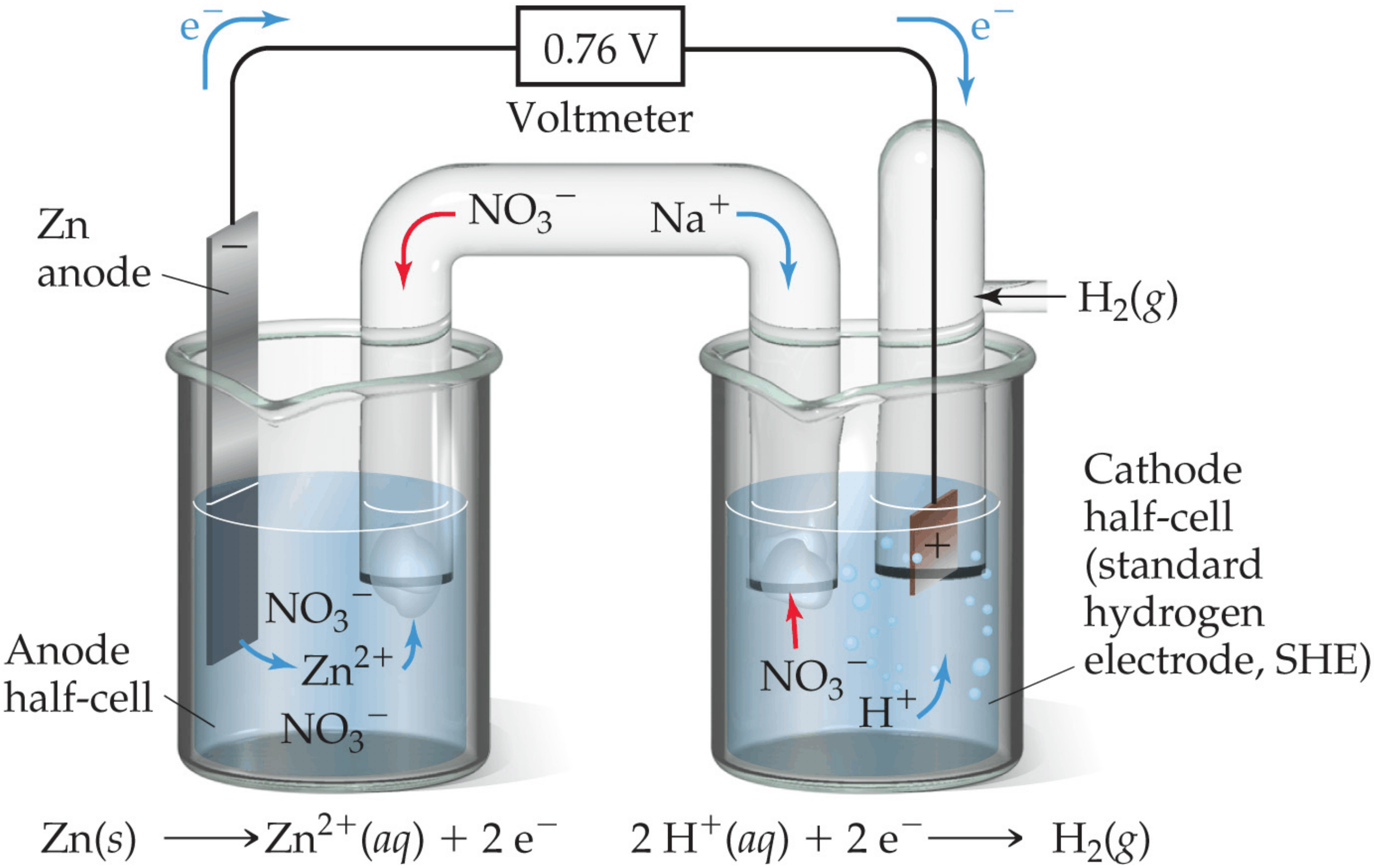
$$E^{o}_{H_2} = 0.00\ V$$



More positive
Cathode (reduction)
E°_{red}(cathode)
E°_{red} (V)
$E^\circ_{cell} = E^\circ_{red}(\text{cathode}) - E^\circ_{red}(\text{anode})$
E°_{red}(anode)
Anode (oxidation)
More negative

TABLE 20.1 • Standard Reduction Potentials in Water at 25 °C

E°_{red} (V)	Reduction Half-Reaction
+2.87	$F_2(g) + 2e^- \longrightarrow 2F^-(aq)$
+1.51	$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l)$
+1.36	$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$
+1.33	$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$
+1.23	$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l)$
+1.06	$Br_2(l) + 2e^- \longrightarrow 2Br^-(aq)$
+0.96	$NO_3^-(aq) + 4H^+(aq) + 3e^- \longrightarrow NO(g) + 2H_2O(l)$
+0.80	$Ag^+(aq) + e^- \longrightarrow Ag(s)$
+0.77	$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$
+0.68	$O_2(g) + 2H^+(aq) + 2e^- \longrightarrow H_2O_2(aq)$
+0.59	$MnO_4^-(aq) + 2H_2O(l) + 3e^- \longrightarrow MnO_2(s) + 4OH^-(aq)$
+0.54	$I_2(s) + 2e^- \longrightarrow 2I^-(aq)$
+0.40	$O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$
+0.34	$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$
0 [defined]	$2H^+(aq) + 2e^- \longrightarrow H_2(g)$
−0.28	$Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)$
−0.44	$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$
−0.76	$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$
−0.83	$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$
−1.66	$Al^{3+}(aq) + 3e^- \longrightarrow Al(s)$
−2.71	$Na^+(aq) + e^- \longrightarrow Na(s)$
−3.05	$Li^+(aq) + e^- \longrightarrow Li(s)$


e⁻
0.76 V
Voltmeter
e⁻
Zn
anode
NO_3^-
Na^+
$H_2(g)$
Cathode
half-cell
(standard
hydrogen
electrode, SHE)
NO_3^-
Anode
half-cell
Zn^{2+}
NO_3^-
NO_3^-
H^+
$Zn(s) \longrightarrow Zn^{2+}(aq) + 2\,e^-$
$2\,H^+(aq) + 2\,e^- \longrightarrow H_2(g)$

D) Strengths of Ox. & Red. Agents

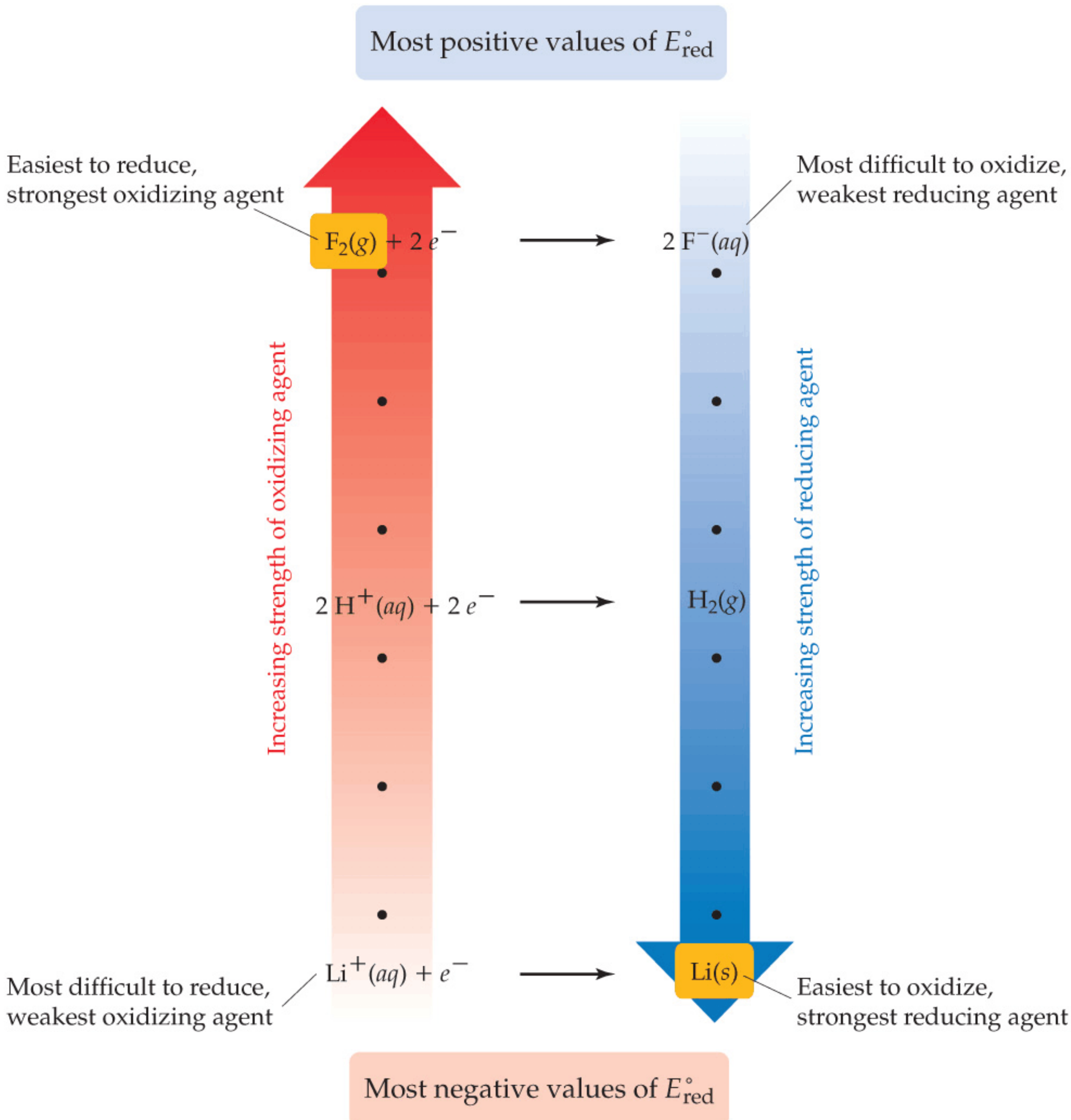
Arranged in table w. greatest tendency for red. at top

Strongest ox. agents are at the upper left (F_2, $S_2O_8^{2-}$, H_2O_2)

Strongest red. agents are at the lower right (Li, Na, Mg, Al)

Note

For a spont. rxn the stronger ox. & red. agents will be the reactants


Most positive values of E°_{red}
Easiest to reduce, strongest oxidizing agent
Most difficult to oxidize, weakest reducing agent
$F_2(g) + 2e^- \rightarrow 2F^-(aq)$
Increasing strength of oxidizing agent
Increasing strength of reducing agent
$2H^+(aq) + 2e^- \rightarrow H_2(g)$
$Li^+(aq) + e^- \rightarrow Li(s)$
Most difficult to reduce, weakest oxidizing agent
Easiest to oxidize, strongest reducing agent
Most negative values of E°_{red}

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−3.05	$Li^+(aq) + e^- \longrightarrow Li(s)$

1) Ex 1 : Which will be the stronger red. agent under standard conditions, Sn^{2+} (to Sn^{4+}) or Fe (to Fe^{2+})

	E^{o}_{red} (V)
$Sn^{4+}(aq) + 2\,e^{-} \longrightarrow Sn^{2+}(aq)$	+ 0.154
$Fe^{2+}(aq) + 2\,e^{-} \longrightarrow Fe(s)$	− 0.440

E) Calc. Cell emf's from Std. Pot.

		E^o_{red} (V)
$Pb^{2+}(aq) + 2\,e^- \longrightarrow Pb(s)$		– 0.13
$Ag^{+}(aq) + e^- \longrightarrow Ag(s)$		+ 0.80

1) rxn. is spont. w. stronger red. agent (one most easily ox.) on left (as reactant), Pb

Reverse of Pb electrode rxn.

NOTE: For a voltaic cell the cathode must be rxn. w. more + E^o_{red}

- Ag electrode in this case

$$Pb(s) \longrightarrow Pb^{2+}(aq) + 2\,e^-$$

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

2) Multiply rxn. 2 (Ag rxn) by 2 to balance the e^-

E^o_{red} NOT multiplied by factor

- intensive quantity

$$Pb(s) \longrightarrow Pb^{2+}(aq) + 2\,e^-$$

$$2\,Ag^+(aq) + 2\,e^- \longrightarrow 2\,Ag(s)$$

3) Add eqns to get overall cell rxn

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

$$Pb(s)\,|\,Pb^{2+}(aq)\,\|\,Ag^+(aq)\,|\,Ag(s)$$

4) Calc. cell potential, E^o_{cell}

$$E^o_{cell} = E^o_{cathode} - E^o_{anode}$$

$$= E^o_{Ag} - E^o_{Pb}$$

V) Equilibrium Constants from emf's

$$\Delta G^\circ = -nFE^\circ_{cell}$$

Also,

$$\Delta G^\circ = -RT\ln K$$

$$\therefore \quad nFE^\circ_{cell} = RT\ln K$$

$$E^\circ_{cell} = \frac{RT}{nF}\ln K$$

or

$$E^\circ_{cell} = \frac{2.303\,RT}{nF}\log K$$

At 25°C

$$E^\circ_{cell} = \frac{0.0592}{n}\log K \quad \text{(in volts)}$$

A) Ex's

1) Calc. ΔG° at 25°C for the Pb - Ag cell.

$$\Delta G^\circ = -nFE^\circ$$

2) Calc. the equil. constant K.

$$E^\circ_{cell} = \frac{0.0592}{n} \log K$$

B) **Ex 2** : What are $\Delta G°$ and K for the following cell?

$$Al(s) \,|\, Al^{3+}(aq) \,||\, Pb^{2+}(aq) \,|\, Pb(s)$$

	$E°$
$Al^{3+} + 3e^- \longrightarrow Al$	-1.66
$Pb^{2+} + 2e^- \longrightarrow Pb$	-0.13

VI) Dependence of emf on Conc.

A) Nernst Equation

$$\Delta G = \Delta G^\circ + RT \ln Q$$

$$-nFE_{cell} = -nFE^\circ_{cell} + RT \ln Q$$

$$E_{cell} = E^\circ_{cell} - \frac{RT}{nF} \ln Q$$

At 25°C,

$$E_{cell} = E^\circ_{cell} - \frac{0.0592}{n} \log Q$$

(in volts)

1) Ex : Determine the voltage of the following cell:

$Cr | Cr^{3+} (0.010 M) || Pb^{2+} (1.00 M) | Pb$

B) Electrode Pot. for NonStandard Conditions

Can use the Nernst eqn to find the electrode pot. when conc. is not 1 M &/or pressure is not 1 atm

1) Ex: what is the pot. of the iron electrode $Fe^{2+}(aq) | Fe(s)$ when the Fe^{2+} conc. is 1.0×10^{-4} M ?

$$Pt | H_2(1\,atm) | H^+(1\,M) || Fe^{2+}(1.0\times10^{-4}\,M) | Fe(s)$$

$$E_{cell} = E(Fe^{2+}/Fe) - E^\circ(H^+/H_2)$$

$$= E(Fe^{2+}/Fe)$$

Using Nernst eqn.,

$$E(Fe^{2+}|Fe) = E^{\circ}(Fe^{2+}|Fe) - \frac{0.0592}{n} \log Q$$

To find n & exp. for Q write overall rx.

$$Fe^{2+}(aq) + H_2(g) \rightleftharpoons Fe(s) + 2H^+(aq)$$

$n = 2$ &

$$Q = \frac{[H^+]^2}{[Fe^{2+}]\, P_{H_2}} = \frac{1^2}{[Fe^{2+}]\cdot 1} = \frac{1}{[Fe^{2+}]}$$

$$\therefore\ E(Fe^{2+}|Fe) = E^{\circ}(Fe^{2+}|Fe) - \frac{0.0592}{2} \log \frac{1}{[Fe^{2+}]}$$

$$= -0.41 - 0.1184$$

$$= -0.53\ V$$

2) Ex : Determine unknown conc. of Cd^{2+}.

$$Cd|Cd^{2+}(aq, ?M) \| Ag^{+}(1M)|Ag$$

$$Cd + 2Ag^{+} \longrightarrow Cd^{2+} + 2Ag$$

measure $E_{cell} = 1.44\,V$

$$E_{cell} = E^{o}_{cell} - \frac{0.0592}{n} \log \frac{[Cd^{2+}]}{[Ag^{+}]^{2}}$$

$$1.44 = 1.20 - \frac{0.0592}{2} \log [Cd^{2+}]$$

$$\log [Cd^{2+}] = -8.11$$

$$[Cd^{2+}] = 7.8 \times 10^{-9}\,M$$

c) Determination of pH

$Pt \mid H_2(1\ atm) \mid H^+(\text{test soln}) \parallel H^+(1M) \mid H_2(1\ atm) \mid Pt$

E_{cell} is due to test soln. half-cell

$$\frac{1}{2} H_2(1\ atm) \rightleftharpoons H^+(\text{test soln.}) + e^-$$

$$E_{cell} = -0.0592 \log[H^+] \quad , 25^\circ C$$

or

$$pH = \frac{E_{cell}}{0.0592}$$

VII) Practical Applications

A) Corrosion Protection

Iron rusts

$Fe \rightarrow Fe^{2+} + 2e^-$ ox.

Place Fe in contact w. a more active metal (more easily oxidized)

Fe/Fe^{2+} becomes cathode

Metal becomes anode

Cathodic Protection

1) Underground Pipe

Fe pipe connected to Mg or Zn rod

$$Mg + Fe^{2+} \rightarrow Mg^{2+} + Fe$$

2) Galvanized Iron

coat w. Zn

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

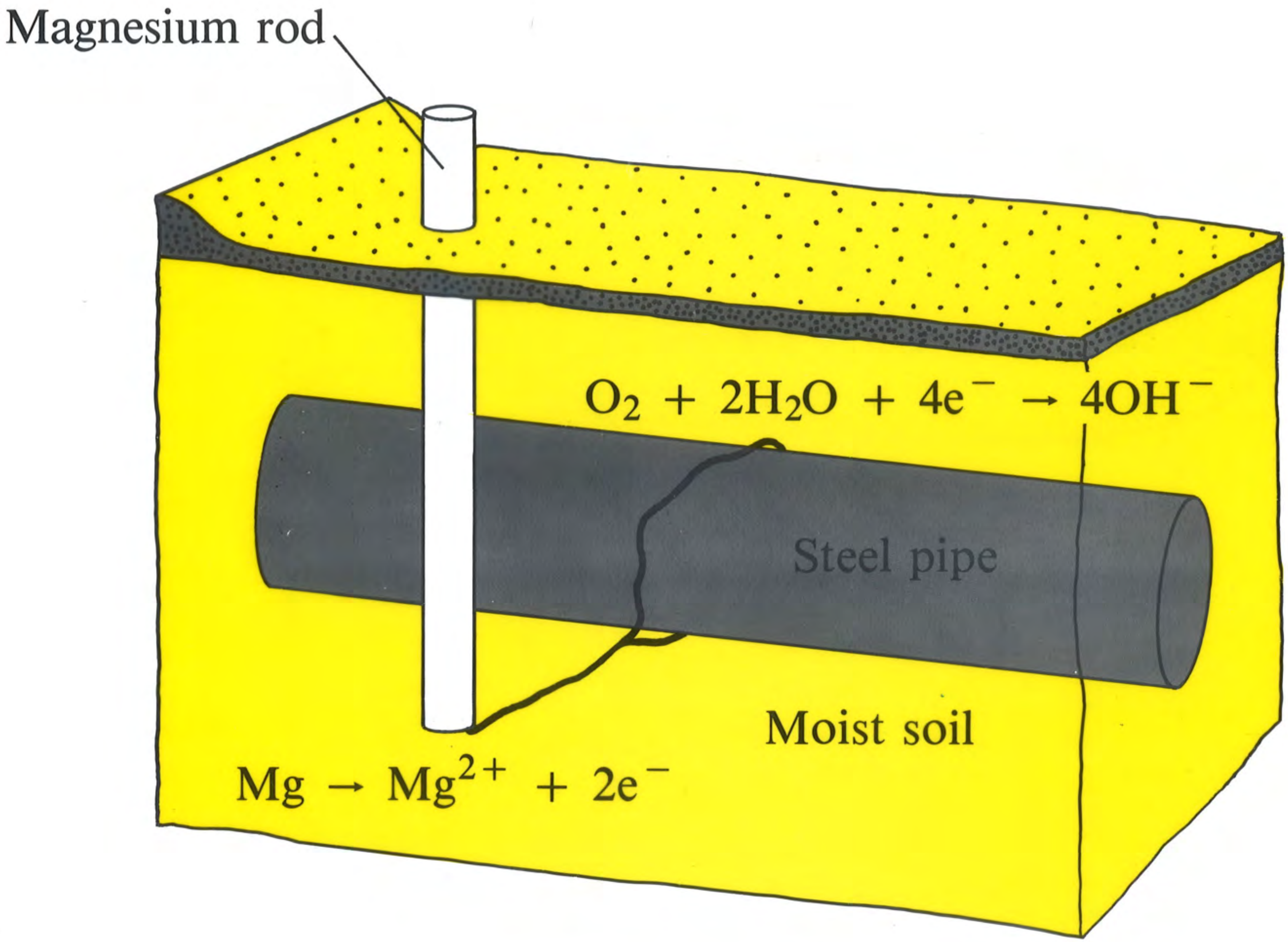

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Figure 19.17 Cathodic protection of a buried steel pipe

B) Fuel Cells

Convert energy of combustion directly into electrical energy

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$$

$$C \,|\, H_2(g) \,|\, OH^-(aq) \,|\, O_2(g) \,|\, C$$

anode : $(H_2 + 2OH^- \rightarrow 2H_2O + 2e^-)2$

cathode : $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

$$2H_2 + O_2 \rightarrow 2H_2O$$

60-70 % efficient

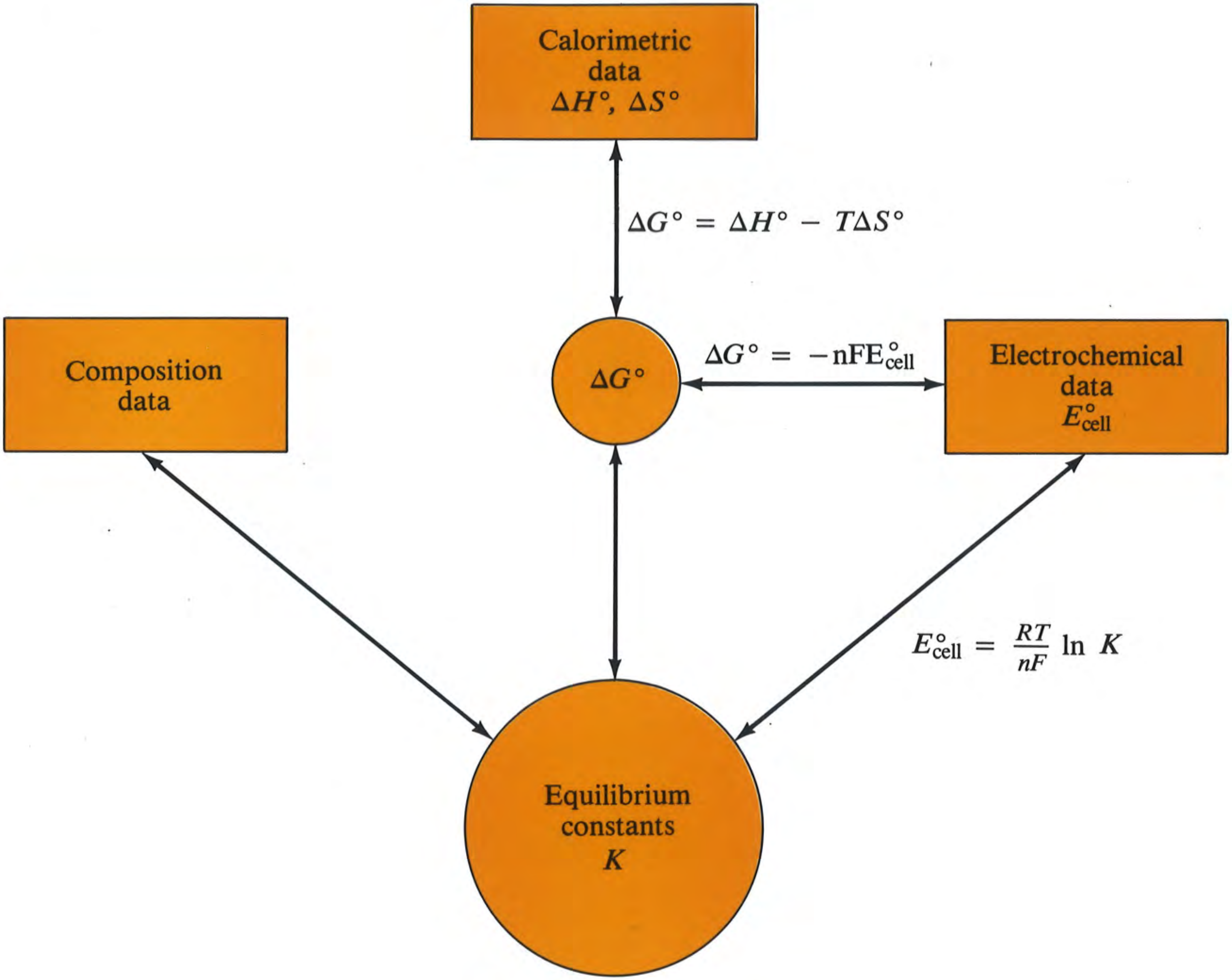

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Figure 19.6 Relationships among K, ΔG°, and E°_{cell}

IX) Electrolytic Cells

Energy from external source is used to bring about a non spont. chem. rx.

Cell is driven by a battery

- Acts as an e^- pump
  - pushes e^- onto one electrode & pulls them from another

A) Electrolysis of Molten NaCl

	E° (V)
$Cl_2 + 2e^- \rightarrow 2Cl^-$	$+1.36$
$Na^+ + e^- \rightarrow Na$	-2.71

anode (ox.): $2Cl^- \rightarrow Cl_2 + 2e^-$

cathode (red.): $2(Na^+ + e^- \rightarrow Na)$

$$2\,NaCl(l) \rightarrow 2\,Na(s) + Cl_2(g)$$

1) E°_{cell}

$$E^\circ_{cell} = E^\circ_{cat} - E^\circ_{an}$$

$$= E^\circ_{Na} - E^\circ_{Cl_2}$$

$$= (-2.71) - (+1.36)$$

$$= -4.07\ V$$

Non spont.

Note: sign convention for eletrodes is opposite that for voltaic cells

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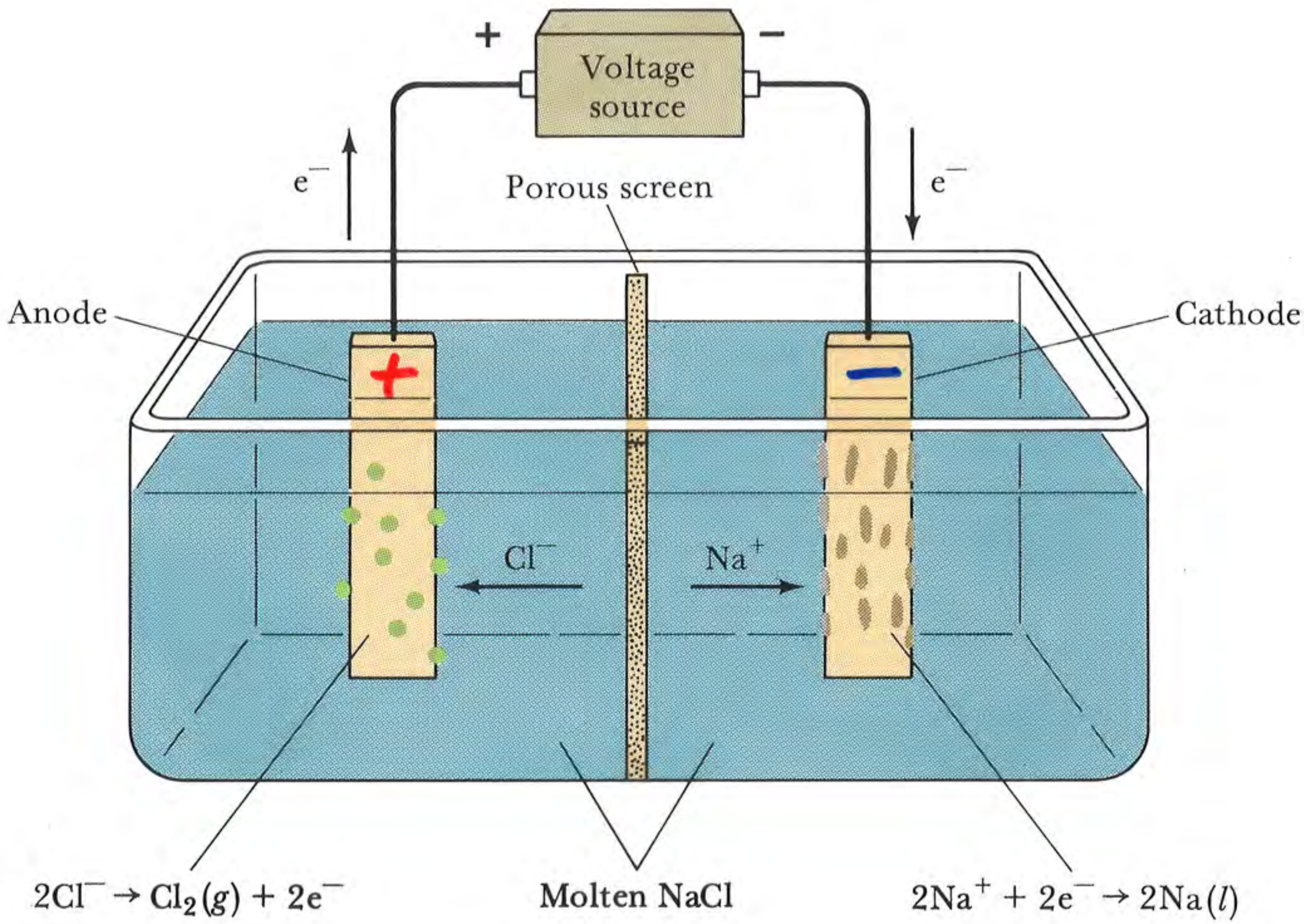
Figure 20.16 Electrolysis of molten sodium chloride



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X) Stoichiometry of Electrolysis

How much product is formed?
How long will it take?

$1\ C = 1\ A \cdot s$

$1\ F = 96{,}500\ C/\text{mole}\ e^-$

A current of 0.50 A flowing for 84 seconds gives a charge of,

$0.50\ A \times 84\ s = 42\ C$

A) Time and Amount

1) Ex: Chrome-plate an object. How long would it take to deposit 35.5g Cr from a soln. of $CrCl_3$ at a current of 6.00 A?

$$Cr^{3+} + 3e^- \rightarrow Cr \quad \text{(cathode)}$$

3 mole e^- req. for each mole Cr

a) How fast does this occur?

$$6.00\,A = 6.00\,C/s$$

b) How many grams of Cl_2 are produced?

B) Electrical Work

1) Voltaic Cell

$$w_{max} = -nFE_{cell}$$

$-w_{max}$ ($w_{max} < 0$)

$\Longrightarrow$ spont.

(max work obtainable)

2) Electrolytic Cell

Non spont. ($\Delta G > 0$, $E < 0$)

– supply external potential

$$w = nFE_{ext}$$

surr. doing work on system

3) Units

Electrical work usually expressed in energy units of

watts x time

$$1\ W = 1\ J/s$$

electric utilities use kW-hour

$$1\ kWh = (1000\ W)(1\ hr)\left(\frac{3600\ s}{1\ hr}\right)\left(\frac{1\ J/s}{1\ W}\right)$$

$$= 3.6 \times 10^6\ J$$

4) Ex: What applied emf is required to produce 2.0×10^3 kg of Al by electrolysis of Al^{3+} if 1.0×10^4 kWh of electricity is used?