Electrochemistry Electrochemistry deals with reactions

All chemical reactions can be categorized into:

1. acid-base reaction (involve proton transfer)
2. Precipitation reaction (involve the formation of precipitates)
3. Oxidation-reduction (involve the electron transfer)

Oxidation-reduction reactions: involve the transfer of

Oxidation: the chemical reaction in which a substance electron is called an oxidation
Reduction: the chemical reaction in which a substance electron is called a reduction

The substance that loses electrons (i.e., the one undergoing oxidation) is called the agent
The substance that gains electrons (i.e., the one undergoing reduction) is called the agent

Oxidation numbers:

An oxidation number is a number (can be 0,+,or-) assigned to each atom (in any substance) in a oxidation-reduction reaction, That reflects whether the atom has fewer(+), more(-) or the same (0) number of electrons as an uncombined neutral atom.

Rules for assigning oxidation numbers

1. The oxidation number of an element in its natural state is 0
   Ex: $Na_{(s)}$, $Ag_{(s)}$,$Hg_{(l)}$,$O_{2(g)}$,$H_{2(g)}$ →0
2. The oxidation number of a monatomic ion is the same as its ionic charge
   Ex: Na^+ →1, Cl^- →-1, Fe^{2+} →+2, F^- →-1
3. In most compounds containing oxygen, the oxidation number of oxygen is -2
   Ex: MgO,SO_2,SO_3,CO,CO_2
   the exception: peroxide,O_2^{2-}, the oxidation number is -1
   Ex: H_2O_2, Na_2O_2
4. In most compounds containing hydrogen, the oxidation number of hydrogen is +1
   Ex: HCl, NH_3, H_2O,CH_4
   the exception: hydride, H^-, the oxidation number is -1
   Ex: LiH, NaH
5. The sum of the oxidation numbers must be zero for electrically neutral compounds. For polyatomic ions, the sum of the oxidation numbers must be equal to the charge of the ion.
   Ex: H_2O → sum of the oxidation number = 0; CrO_4^{2-} → sum of the oxidation number = -2

(a) Calculate the oxidation number for C in CO_2

(d) Calculate the oxidation number for S in $S_2O_3^{2-}$

(b) Calculate the oxidation number for P in H_3PO_4

(c) Calculate the oxidation number for Cl in ClO_3^-

Redox reaction

$A + B \rightarrow A^+ + B^-$

Half-rxn:

$A \rightarrow A^+ + e^-$ (oxidation half reaction, electron loss)

$B + e^- \rightarrow B^-$ (Reduction half reaction, electron gain)

A	**B**
Lose electron	**G**ain electron
Oxidation , O.N. increase	**R**eduction, O.N. decrease
Reducing reagent	**O**xidation reagent
Anode	**C**athode

$2\ K_{(s)} \quad + \quad Cl_{2(g)} \rightarrow \quad 2KCl$

$SiCl_{4(l)} \quad + \quad 2H_2O\ _{(g)} \rightarrow \quad 4HCl_{(aq)} + \quad SiO_{2\ (s)}$

$CH_{4(g)} \quad + \quad 2O_{2(g)} \rightarrow \quad CO_{2(g)} + \quad 2H_2O_{(g)}$

Balancing oxidation reduction reactions:

Ex:

$$Cu_{(s)} + HNO_{3(aq)} \rightarrow Cu(NO_3)_{2(aq)} + NO_{2(g)} + H_2O_{(l)}$$

Ex:

$$NaCl + H_2SO_4 + MnO_2 \rightarrow Na_2SO_4 + MnCl_2 + H_2O + Cl_2$$

Balancing redox reactions in acidic/basic aqueous solution: do not mix and match!!

Acidic: H^+/H_2O

basic: $H_2O/2OH^-$

Balance the following reaction in **acidic aqueous** solutions

$$Fe^{2+}_{(aq)} + MnO_4^-{}_{(aq)} \rightarrow Fe^{3+}_{(aq)} + Mn^{2+}_{(aq)}$$

	need	**add**
Acidic aqueous solution	H O	$H^+ \leftrightarrow H_2O$ $H_2O \leftrightarrow 2H^+$
basic aqueous solution	H O	$H_2O \leftrightarrow OH^-$ $2OH^- \leftrightarrow H_2O$

1. Write 2 half-reaction
2. Balance all atoms using H_2O,H^+, or OH^- as needed
3. Balance charges in both half reactions using e^-
4. Add the two half reactions with same e^- gained or lost
5. Check charge balance on both side

Balance the following reaction in **basic aqueous** solutions

$Zn_{(aq)} \quad + \quad HgO_{(aq)} \rightarrow ZnO_2^{2-}{}_{(aq)} \quad + \quad Hg_{(aq)}$

	need	**add**
Acidic aqueous solution	H O	$H^+ \leftrightarrow H_2O$ $H_2O \leftrightarrow 2H^+$
basic aqueous solution	H O	$H_2O \leftrightarrow OH^-$ $2OH^- \leftrightarrow H_2O$

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   using e^-
4. Add the two half reactions
   with same e^- gained or lost
5. Check charge balance on both side

$Ag_{(s)} + CN^-_{(aq)} + O_{2(g)} \rightarrow Ag(CN)_2^-{}_{(aq)}$ in basic solution

	need	add
Acidic aqueous solution	H O	$H^+ \leftrightarrow H_2O$ $H_2O \leftrightarrow 2H^+$
basic aqueous solution	H O	$H_2O \leftrightarrow OH^-$ $2OH^- \leftrightarrow H_2O$

1. Write 2 half-reaction
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$Br_{2(g)} \rightarrow BrO_3^-{}_{(aq)} + Br^-_{(aq)}$ in acidic solution

General reaction

$Zn_{(s)} + CuSO_{4(aq)} \rightarrow ZnSO_{4(aq)} + Cu_{(s)}$ $\Delta G<0$ spontaneous

Complete ionic reaction

$Zn_{(s)} + Cu^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)} + Cu_{(s)}$

Net ionic reaction

$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$ Half reaction

Redox couple: **oxidized form/reduced form**

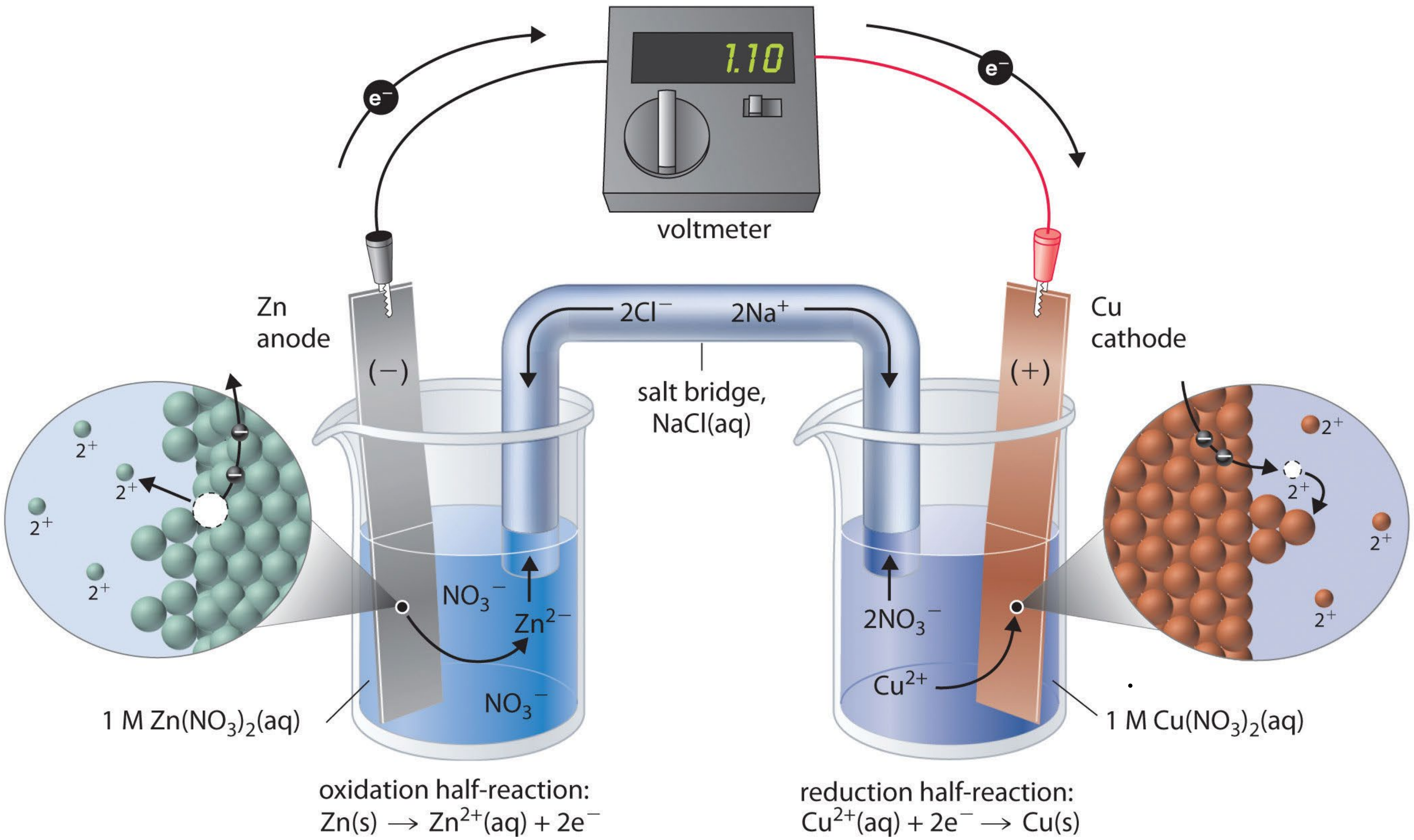
Electrochemical cells

An electrochemical cell is a device in which
an electric current (flow of electrons) is either produced by a spontaneous chemical reaction or
is used to bring about a non-spontaneous reaction

Galvanic cells (voltaic cells)

A Galvanic cells is an electrochemical cell is a device in which a spontaneous chemical reaction is used to generate an electric current → battery

$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$ $\Delta G<0$ spontaneous



Anode	Cathode
Oxidation Occurs	Reduction Occurs
Electrons are pushed into wire	Electrons are pulled in from the wire
- sign	+ sign

Cell notations

$Zn_{(s)}$ + $Cu^{2+}{}_{(aq)} \rightarrow$ $Zn^{2+}{}_{(aq)}$ + $Cu_{(s)}$

Redox couple: $Zn^{2+}{}_{(aq)}/Zn_{(s)}$
$Cu^{2+}{}_{(aq)}/Cu_{(s)}$

Electrode: Reactant | Product (two different phase) ; Reactant, Product (same phase)

Anode: $Zn_{(s)}$ | $Zn^{2+}{}_{(aq)}$

Cathode: $Cu^{2+}{}_{(aq)}$ | $Cu_{(s)}$

Cell notation: $Zn_{(s)}$ | $Zn^{2+}{}_{(aq)}$ || $Cu^{2+}{}_{(aq)}$ | $Cu_{(s)}$

Electrodes:

- Zn electrode
- Cu electrode
- Hydrogen electrode

Hydrogen electrode

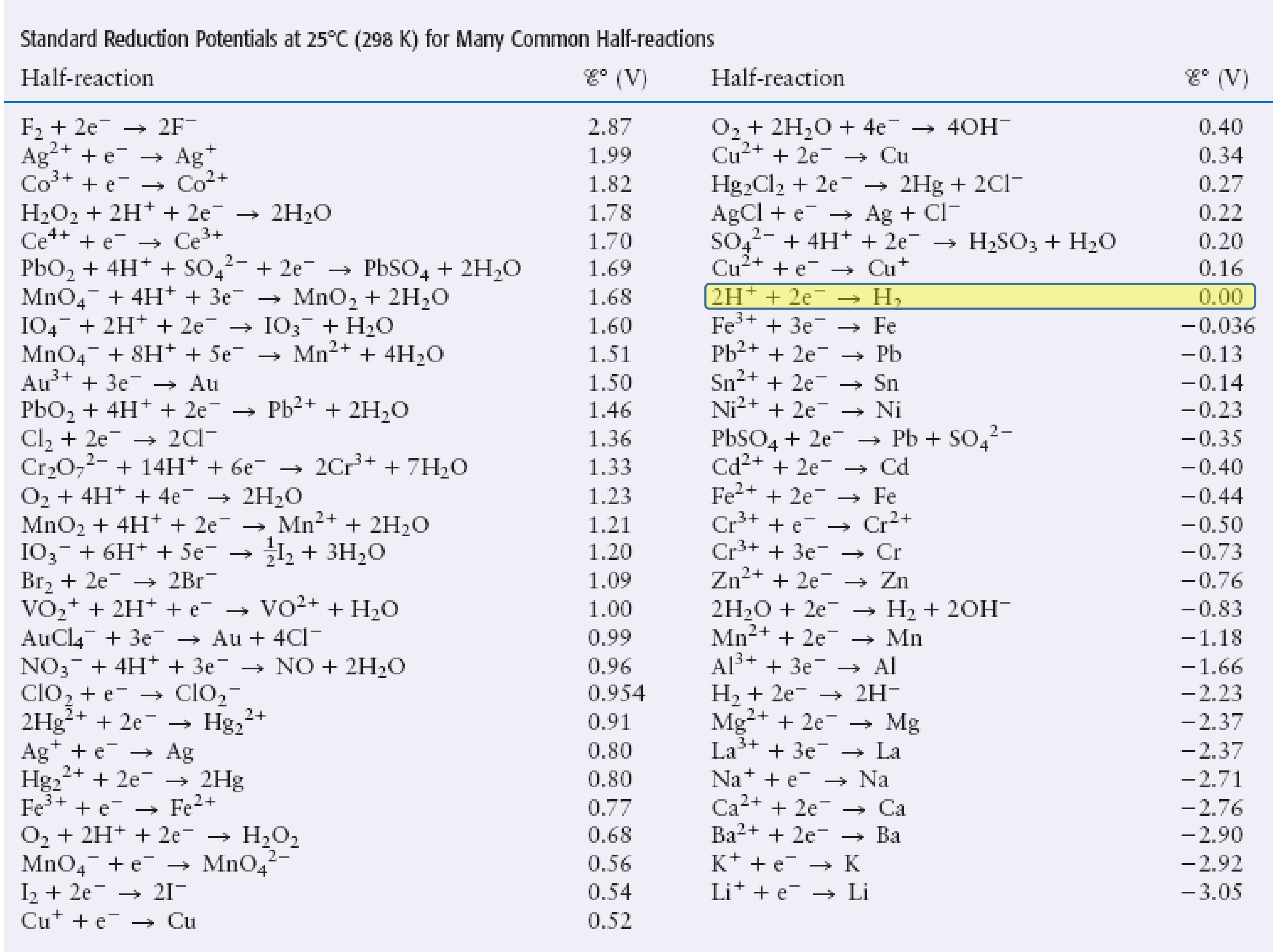
Anode: $H_{2(g)} \rightarrow 2H^{+} + 2e^{-}$

Cathode: $2H^{+} + 2e^{-} \rightarrow H_{2(g)}$

Anode: $Pt_{(s)} | H_{2(g)} | H^{+}_{(aq)}$

Cathode: $H^{+}_{(aq)} | H_{2(g)} | Pt_{(s)}$

Standard Reduction Potentials



Standard Reduction Potentials at 25°C (298 K) for Many Common Half-reactions

Half-reaction	ℰ° (V)	Half-reaction	ℰ° (V)
$F_2 + 2e^- \rightarrow 2F^-$	2.87	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	0.40
$Ag^{2+} + e^- \rightarrow Ag^+$	1.99	$Cu^{2+} + 2e^- \rightarrow Cu$	0.34
$Co^{3+} + e^- \rightarrow Co^{2+}$	1.82	$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$	0.27
$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	1.78	$AgCl + e^- \rightarrow Ag + Cl^-$	0.22
$Ce^{4+} + e^- \rightarrow Ce^{3+}$	1.70	$SO_4^{2-} + 4H^+ + 2e^- \rightarrow H_2SO_3 + H_2O$	0.20
$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$	1.69	$Cu^{2+} + e^- \rightarrow Cu^+$	0.16
$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$	1.68	$2H^+ + 2e^- \rightarrow H_2$	0.00
$IO_4^- + 2H^+ + 2e^- \rightarrow IO_3^- + H_2O$	1.60	$Fe^{3+} + 3e^- \rightarrow Fe$	−0.036
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	1.51	$Pb^{2+} + 2e^- \rightarrow Pb$	−0.13
$Au^{3+} + 3e^- \rightarrow Au$	1.50	$Sn^{2+} + 2e^- \rightarrow Sn$	−0.14
$PbO_2 + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2H_2O$	1.46	$Ni^{2+} + 2e^- \rightarrow Ni$	−0.23
$Cl_2 + 2e^- \rightarrow 2Cl^-$	1.36	$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$	−0.35
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	1.33	$Cd^{2+} + 2e^- \rightarrow Cd$	−0.40
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	1.23	$Fe^{2+} + 2e^- \rightarrow Fe$	−0.44
$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	1.21	$Cr^{3+} + e^- \rightarrow Cr^{2+}$	−0.50
$IO_3^- + 6H^+ + 5e^- \rightarrow \frac{1}{2}I_2 + 3H_2O$	1.20	$Cr^{3+} + 3e^- \rightarrow Cr$	−0.73
$Br_2 + 2e^- \rightarrow 2Br^-$	1.09	$Zn^{2+} + 2e^- \rightarrow Zn$	−0.76
$VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$	1.00	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	−0.83
$AuCl_4^- + 3e^- \rightarrow Au + 4Cl^-$	0.99	$Mn^{2+} + 2e^- \rightarrow Mn$	−1.18
$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$	0.96	$Al^{3+} + 3e^- \rightarrow Al$	−1.66
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$2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+}$	0.91	$Mg^{2+} + 2e^- \rightarrow Mg$	−2.37
$Ag^+ + e^- \rightarrow Ag$	0.80	$La^{3+} + 3e^- \rightarrow La$	−2.37
$Hg_2^{2+} + 2e^- \rightarrow 2Hg$	0.80	$Na^+ + e^- \rightarrow Na$	−2.71
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.77	$Ca^{2+} + 2e^- \rightarrow Ca$	−2.76
$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	0.68	$Ba^{2+} + 2e^- \rightarrow Ba$	−2.90
$MnO_4^- + e^- \rightarrow MnO_4^{2-}$	0.56	$K^+ + e^- \rightarrow K$	−2.92
$I_2 + 2e^- \rightarrow 2I^-$	0.54	$Li^+ + e^- \rightarrow Li$	−3.05
$Cu^+ + e^- \rightarrow Cu$	0.52		

Standard Oxidation Potentials

Cell potential, voltage, electromotive force (E_{cell})

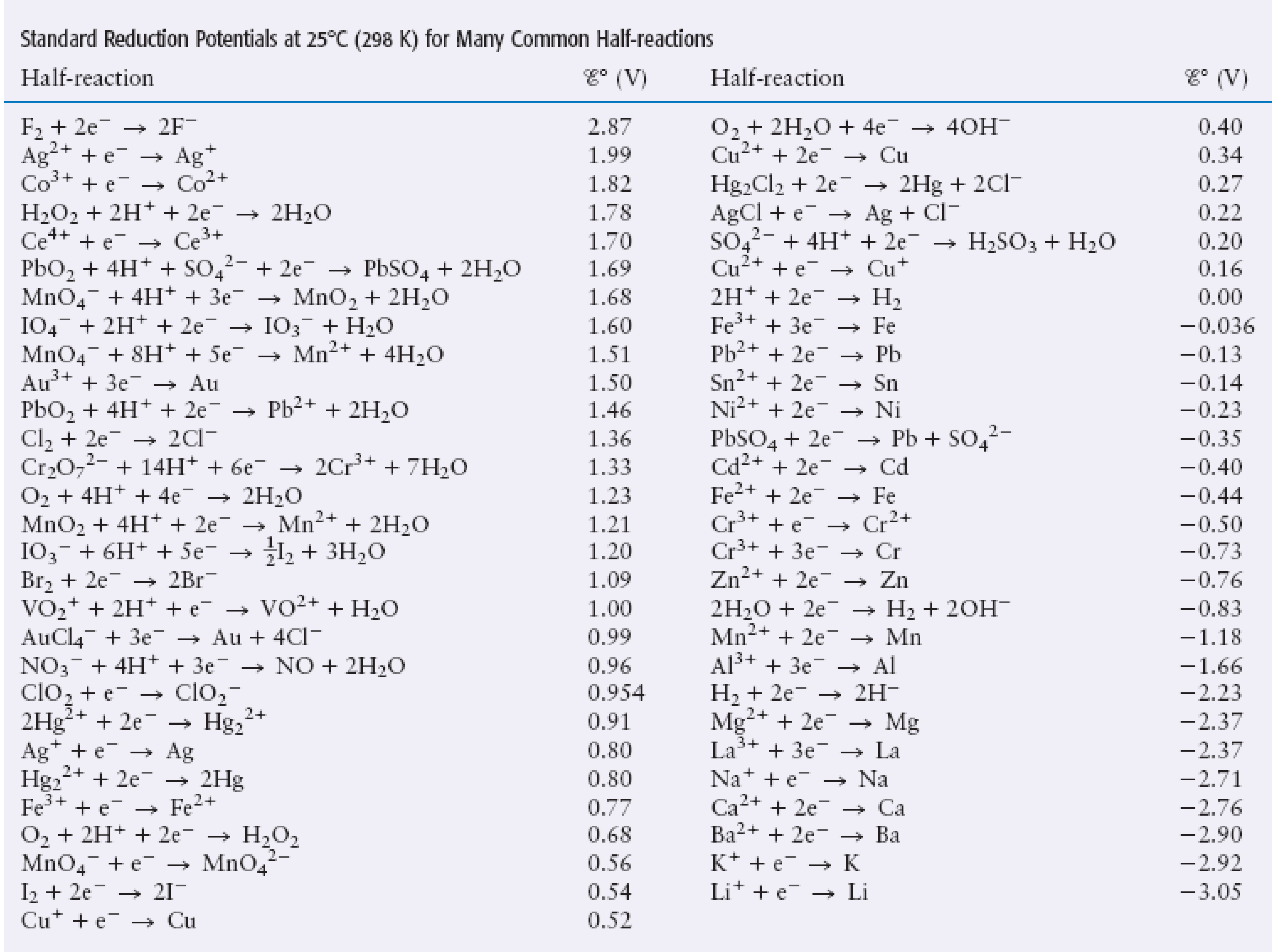
A measure of the ability of a cell to push and pull electrons through a circuit.

Unit: V (volts)

$Zn_{(s)} \mid Zn^{2+}_{(aq)} \mid\mid Cu^{2+}_{(aq)} \mid Cu_{(s)}$ E_{cell}= 1.10V

$$E^0_{cell} = E^0_{cathode} + E^0_{anode} = E^0 + E^0_{oxi}$$

$Fe_{(s)} \mid Fe^{2+}_{(aq)} \mid\mid Ag^{+}_{(aq)} \mid Ag_{(s)}$ E_{cell}= 1.24V



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$Ce^{4+} + e^- \rightarrow Ce^{3+}$	1.70	$SO_4^{2-} + 4H^+ + 2e^- \rightarrow H_2SO_3 + H_2O$	0.20
$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$	1.69	$Cu^{2+} + e^- \rightarrow Cu^+$	0.16
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$Zn_{(s)}$ | $Zn^{2+}_{(aq)}$ || $H^{+}_{(aq)}$ | $H_{2(g)}$ E_{cell}= 0.76V

$Mn_{(s)}$ | $Mn^{2+}_{(aq)}$ || $Ag^{+}_{(aq)}$ | $Ag_{(s)}$ E_{cell}= 1.98V

Ex: determine the E_{cell} of the following redox reaction:

$2\ Cu^{+}_{(aq)} + Ca_{(s)} \rightarrow 2Cu(s) + Ca^{2+}_{(aq)}$ E_{cell}= 3.28V

Is an acidified permanganate solution a more powerful oxidizing agent than an acidified dichromate solution?

Can aqueous $KMnO_4$ be used to oxidize iron(II) to iron(III) under standard conditions in acidic solution?

E_{cell} and ΔG

E$_{cell}$ spontaneity

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

n: number of moles of electrons transferred in the rxn as given by the balanced equation

F: Faraday's constant. (the charges per mole of electrons) = 9.6485×10^4 C/mol (C:coulumbs)

$\Delta G < 0$, spontaneous

$E > 0$, spontaneous

$Zn_{(s)} + Cu^{2+} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$

$\boxed{1\ C\ V = 1\ J}$

$N_{2(g)} + 3H_2 \rightarrow 2NH_{3(g)}$ $E^0_{cell} = 0.057V$, what is the **ΔG^0**

E^{o}_{cell} and equilibrium constant K

$$\Delta G^{o} = -\,RT\ \ln K$$

$$\Delta G^{o} = -\,nFE^{o}_{cell}$$

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

$$E^{0}_{cell} = \frac{RT}{nF}\ln K$$

$$\boxed{\frac{RT}{F} = 0.025693\ \mathrm{V}}$$

$$\ln K = \frac{nE^{o}_{cell}}{0.025693}$$

$$E^{0}_{cell} = \frac{0.025693}{n}\ln K$$

Calculate K for the

$$Zn_{(s)} + \quad Cu^{2+} \rightarrow Zn^{2+}_{(aq)} + \quad Cu_{(s)} \qquad E^{o}_{cell} = 1.10V$$

Nernst Equation

The formula for predicting the variation of the cell potential with concentrations and pressures

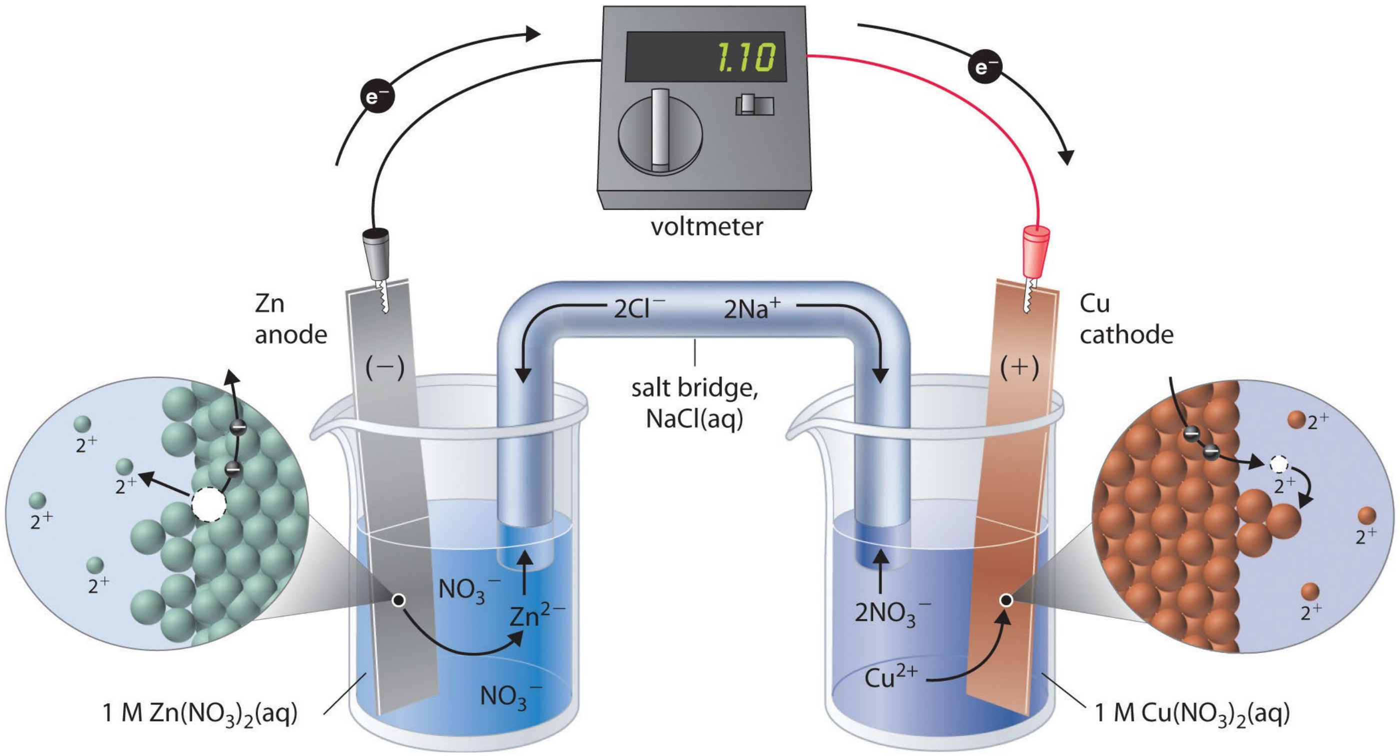
$$\Delta G = \Delta G^o + RT\ \ln Q$$

Calculate the potential at 25C of a galvanic cell:
$Zn_{(s)}\ |\ Zn^{2+}{}_{(aq)}\ ||\ Cu^{2+}{}_{(aq)}\ |\ Cu_{(s)}$, E_{cell}= 1.10V, in which the concentration of $Zn^{2+}{}_{(aq)}$ is 0.10 mol/L and that of the $Cu^{2+}{}_{(aq)}$ ions is 0.0010 mol/L.

$$E_{cell} = E^0{}_{cell} - \frac{RT}{nF}\ln Q$$

$$E_{cell} = E^0{}_{cell} - \frac{0.025693}{n}\ln Q$$

Electrolysis (electrolytic cell)



Over potential

Electro plating

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$Cu^+ + e^- \rightarrow Cu$	0.52		

Predicting the products of electrolysis

The cations are attracted to the cathode
The anions are attracted to the anode

Electrolysis of molten salt

Ex: isolation of Na and Cl_2 by electrolysis of molten NaCl

Electrolysis of mixed molten salt

The **cations** with **less negative** E^0 value (the **stronger oxidizing agent**) is reduced at the **cathode**

The **anions** with **less negative** E^0_{oxi} value (the **stronger reducing agent**) is oxidized at the **anode**

Ex: Predict the products of the electrolysis of a molten mixture of NaCl and AlF_3

Consider a solution containing 0.10 *M* of each of the following: Pb^{2+}, Cu^{2+}, Sn^{2+}, Ni^{2+}, and Zn^{2+}.

Predict the order in which the metals plate out as the voltage is turned up from zero.

Cu^{2+}, Pb^{2+}, Sn^{2+}, Ni^{2+}, Zn^{2+}

Do the metals form on the cathode or the anode? Explain.

Electrolysis of H_2O

Pure water is hard to electrolyze (low conductivity), so a small amount of a non-reactive salt (NaNO3) is added (can be neglected)

H_2O is reduced at the cathode

$$2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH^- \quad \boldsymbol{E^0} = -0.83\ V$$

H_2O is oxidized at the anode:

$$2H_2O_{(l)} \rightarrow O_{2(g)} + 4H^+ + 4e^- \quad \boldsymbol{E^0_{oxi}} = -1.23\ V$$

Electrolysis of aqueous solution

Possible cathode half-reactions (reduction)

1. Reduction of **H_2O**
2. Reduction of **cations** in the solution

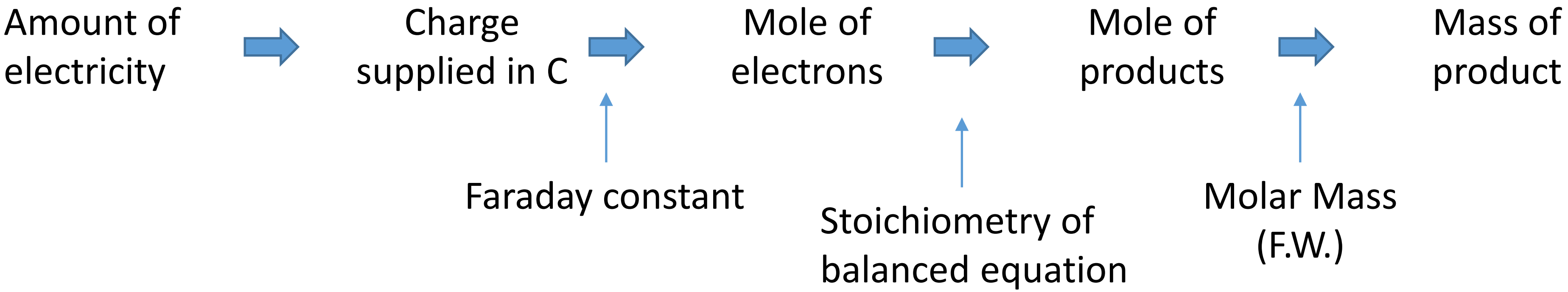
Possible anode half-reactions (oxidation)

1. Oxidation of **H_2O**
2. Oxidation of **active metal electrodes**
3. Oxidation of **anions** in the solution

Predict the products of the electrolysis of a mixture of 1M $NaCl_{(aq)}$ and 1M $KNO_{3(aq)}$ with inert electrodes

Calculating amounts of products of electrolysis

The calculations are based on the Faraday's Law of electrolysis: the number of moles of product formed by an electric current is stoichiometrically equivalent to the number of moles of electrons supplied.



Amount of electricity

Charge supplied in C

Mole of electrons

Mole of products

Mass of product

Faraday constant

Stoichiometry of balanced equation

Molar Mass (F.W.)

Charge supplied (C) = current (A) x time (s)

Moles of electrons (n_e) = charge supplied (C)/F

Moles of product ($n_{product}$) = n_e / n_{ET}

Mass of product = $n_{product}$ x F.W.$_{product}$

Aluminum is produced by electrolysis of its oxide (Al_2O_3) dissolved in molten cryolite (Na_3AlF_6). Calculate the mass of aluminum that can be produced in 1 day in an electrolytic cell operating continuously at 1.0×10^5 A. F.W of Al = 26.98 g/mol.