Electrochemistry

Branch of chemistry dealing with the relation between chemical energy and electrical energy, and inter-conversion of one form into the other.

Redox - Quick Recall

Oxidation = ~~gain~~ loss of electrons (LEO)
Reduction = gain of electrons (GER)
Oxidising agent = the species reduced
Reducing agent = the species oxidised

$$\boxed{Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu}$$ (redox)

Oxidation Number Rules

① Free element : O.N. = 0
② Monatomic ion : O.N. = charge
③ H in compounds : +1 (-1 in hydrides)
④ O in compounds : -2 (peroxide -1)
⑤ F always -1 ; group I = +1 ; II = +2
⑥ Sum of O.N. in neutral compound = 0
⑦ Sum of O.N. in ion = charge of ion

Example : in $KMnO_4$, let O.N. of Mn = x

$$1 + x + 4(-2) = 0 \Rightarrow x = +7$$

Galvanic vs Electrolytic Cells

Galvanic	Electrolytic
Chemical -> electrical	Electrical -> chemical
Spontaneous redox	Non-spontaneous
$dG < 0$	$dG > 0$ (forced)
Two half-cells with salt bridge	One cell with one electrolyte
Anode : -ve ,	Anode : +ve ,
Cathode : +ve	Cathode : -ve
Eg Daniell cell	Eg molten NaCl
(produces current)	(needs external EMF)

Sign Convention

Anode : electrode where OXIDATION occurs

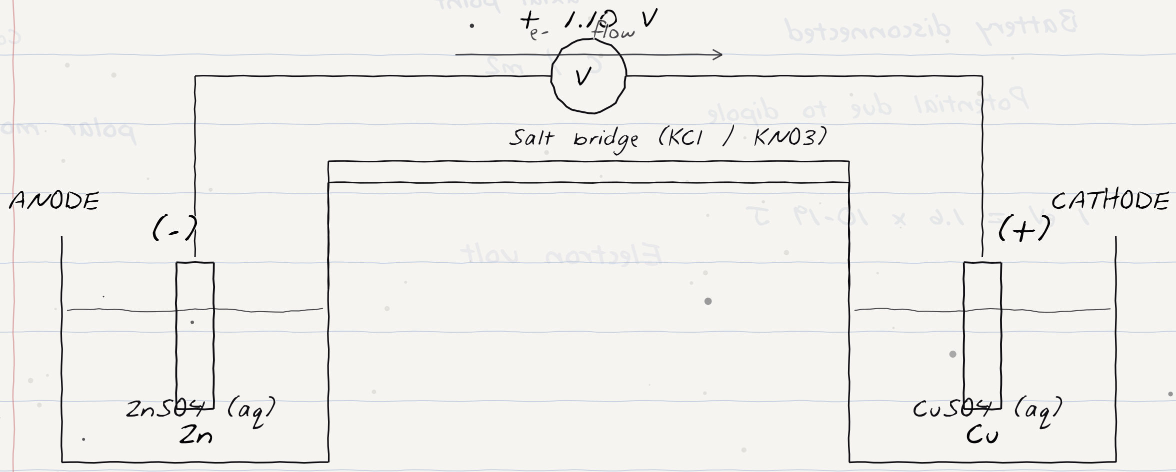
Cathode : electrode where REDUCTION occurs

In a galvanic cell electrons flow from anode -> cathode through external wire. Inside the cell, cations move towards cathode and anions move towards anode.

Galvanic : Cathode = + , Anode =

<- REMEMBER!

Daniell Cell



Half-cell Reactions

Anode (oxidation) : $Zn \rightarrow Zn^{2+} + 2e^-$

Cathode (reduc.) : $Cu^{2+} + 2e^- \rightarrow Cu$

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

$$\boxed{\text{Cathode} = (+), \quad \text{Anode} = (-)}$$ in GALVANIC cell

<-(opposite in electrolytic?)

Cell Notation

Zn	Zn^{2+} (1 M)	Cu^{2+} (1 M)	Cu
anode	electrolyte	electrolyte	cathode

(single bar = phase boundary, double = salt bridge)

Standard Hydrogen Electrode (SHE)

Reference electrode against which all other electrode potentials are measured.

$$\boxed{Pt \quad H_2\ (g,\ 1\ bar) \quad H^+\ (aq,\ 1\ M)}$$

Conditions

① $[H^+] = 1\ M$ (aq)
② $P_{H2} = 1$ bar (gas)
③ Temperature = 298 K (25 deg C)
④ Pt electrode (platinised platinum)

$$\boxed{2\ H^+\ (1\ M) + 2e^- \rightarrow H_2\ (1\ bar)}$$

$$\boxed{E^0(H^+/H_2) = 0.00\ V \quad (\text{by convention})}$$ <- DEFINITIO

Use

Connected to another half-cell as cathode/anode.

Measured EMF directly gives E0 of the other electrode (with proper sign).

Note : modern IUPAC convention = REDUCTION potentials only (sign matches electrode role).

Electrochemical Series

Arrangement of electrodes in order of their standard reduction potentials at 298 K.

Electrode	E^0 / V	
Li^+ / Li	- 3.04	
K^+ / K	- 2.93	stronger
Ca^{2+} / Ca	- 2.87	reducing
Na^+ / Na	- 2.71	agent
Mg^{2+} / Mg	- 2.37	
Al^{3+} / Al	- 1.66	
Zn^{2+} / Zn	- 0.76	
Fe^{2+} / Fe	- 0.44	
H^+ / H_2 (SHE)	0.00	
Cu^{2+} / Cu	+ 0.34	
I_2 / I^-	+ 0.54	
Ag^+ / Ag	+ 0.80	stronger
Br_2 / Br^-	+ 1.09	oxidising
Cl_2 / Cl^-	+ 1.36	agent
F_2 / F^-	+ 2.87	↓

Higher E^0 $\Rightarrow$ stronger oxidising agent (gets reduced more easily). F_2 strongest oxidant, Li strongest reducing agent.

Cell EMF

EMF = potential difference between cathode and anode at zero current.

$$\boxed{E^0_{cell} = E^0_{cathode} - E^0_{anode}}$$

<- both as REDUCTION potentials

If E0_cell > 0 => spontaneous cell reaction

If E0_cell < 0 => non-spontaneous

Worked Example 1

Daniell cell : Zn Zn^{2+} (1 M) Cu^{2+} (1 M)   Cu

Find E0_cell.

Given : $E^0(Cu^{2+}/Cu) = +0.34$ V

$E^0(Zn^{2+}/Zn) = -0.76$ V

Cathode = Cu (higher E0) ; Anode = Zn

$$E^0_{cell} = (+0.34) - (-0.76)$$

$$\boxed{= +1.10 \text{ V}}$$

<- matches voltmeter !

Positive value => spontaneous.

Gibbs Energy & Cell EMF

Max useful work obtainable from a galvanic cell = - dG (at constant T, P).

$$\boxed{dG^0 = - n F E^0_{cell}}$$

<- n = electrons transferred
<- F = 96500 C / mol

Sign matches : E0 > 0 => dG0 < 0 => spontaneous reaction.

Equilibrium Constant

From thermodynamics :

$$dG^0 = - R T \ln K$$

Combining the two :

$$\boxed{- n F E^0_{cell} = - R T \ln K}$$

At T = 298 K, converting ln to log :

$$\boxed{\log K = (n E^0_{cell}) / 0.0591}$$

<- at 298 K

Large E0 => very large K => goes to completion.

Worked Example 2

Calculate K for the Daniell cell.

Given : $E^{0}_{cell} = +1.10\ V$, $n = 2$

Step 1 : write the formula

$$\boxed{\log K = n E^{0}_{cell} / 0.0591}$$

Step 2 : substitute values

$$\begin{aligned} \log K &= (2 \times 1.10) / 0.0591 \\ &= 2.20 / 0.0591 \\ &= \cancel{37.0}\ \ 37.22 \end{aligned}$$

Step 3 : take antilog

$$\boxed{K = 10^{37.22} = 1.66 \times 10^{37}}$$ <- very large K

Interpretation :

K >> 1 => reaction is essentially complete ; nearly all Cu2+ is reduced to Cu(s) and all Zn is oxidised to Zn2+.

Nernst Equation

Cell EMF depends on concentration of ions.

Nernst gave the quantitative dependence.

$$\boxed{E_{cell} = E^0_{cell} - (RT / nF) \ln Q}$$

<- Q = reaction quotient

At T = 298 K, converting ln to log :

$$\boxed{E_{cell} = E^0_{cell} - (0.0591 / n) \log Q}$$ <- 298 K form

For a single electrode

$M^{n+} + n\, e^- \rightarrow M$

$$\boxed{E_{M^{n+}/M} = E^0_{M^{n+}/M} + (0.0591/n) \log [M^{n+}]}$$

Reaction Quotient Q

For : $aA + bB \rightarrow cC + dD$

$$Q = [C]^c [D]^d / [A]^a [B]^b$$

Pure solids/liquids are taken as 1.

Worked Example 3

Daniell cell at 298 K with $[Zn^{2+}] = 0.1$ M, $[Cu^{2+}] = 1.0$ M. Find E_{cell}.

Step 1 : cell reaction & Q

$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$ $(n = 2)$

$$Q = [Zn^{2+}] / [Cu^{2+}]$$
$$= 0.1 / 1.0 = 0.1$$

Step 2 : apply Nernst

$$E_{cell} = 1.10 - (0.0591 / 2) \log (0.1)$$
$$= 1.10 - (0.02955) \times (-1)$$
$$= 1.10 + 0.0296$$

$$\boxed{E_{cell} = +1.13 \text{ V}}$$

<- (slightly higher than E0)

Interpretation :

[Cu2+] >> [Zn2+] => reaction shifts forward by Le Chatelier => EMF higher than at 1 M:1 M.

If [Zn2+] > [Cu2+] then E < E0 (suppressed).

At equilibrium Q = K, E = 0.

Conductance of Electrolytes

Resistance

R = rho (L / A)   (rho = resistivity)

Units : ohm (Ohm) ; rho in ohm cm.

Conductance G

$\boxed{G = 1 / R \qquad \text{unit : } S}$ (siemens)

1 S = 1 ohm^{-1} / mho

Conductivity (kappa)

$\boxed{\text{kappa} = G \times (L / A) = 1 / \text{rho}}$ ~~rho~~ l/A = cell constant

Units : S cm^{-1}

or S m^{-1}

(1 S m-1 = 10-2 S cm-1)

Factors Affecting Conductivity

① Nature of electrolyte : strong > weak

② Concentration of ions (more c -> more kappa)

③ Temperature (T up -> conductivity up)

④ Size + charge of ions

⑤ Viscosity of solvent

Metals : kappa decreases with T (opposite trend).

Molar Conductivity

Conductance of solution containing 1 mole of electrolyte placed between electrodes 1 cm apart.

$$\boxed{\text{Lambda}_m = \text{kappa} \times 1000 / c}$$

<- c in mol / L
<- kappa in S cm-1

Alternative form (V = volume containing 1 mol) :

$$\boxed{\text{Lambda}_m = \text{kappa} \times V}$$

$$\boxed{\text{Units} : \text{S cm}^2 \text{ mol}^{-1}}$$

Worked check

KCl 0.1 M ; kappa = 1.29×10^{-2} S cm^{-1}

$$\text{Lambda}_m = (1.29 \times 10^{-2}) \times 1000 / 0.1$$
$$= 129 \text{ S cm}^2 \text{ mol}^{-1}$$

Equivalent conductivity (out of NCERT but useful) :

$$\text{Lambda}_{eq} = \text{kappa} \times 1000 / n\,c$$

n = number of equivalents per formula unit.

Variation of Lambda_m with Dilution

Two behaviours

① Strong electrolyte : gradual increase

Reason : inter-ionic attractions reduce on dilution.

② Weak electrolyte : steep increase

Reason : degree of dissociation rises sharply with dilution (more ions formed).

Lambda (or Lambda_m) : molar conductivity at infinite dilution (limiting molar conductivity).

For weak electrolytes Lambda_m cannot be found by

Debye-Huckel-Onsager & Kohlrausch

For STRONG electrolytes

Lambda_m varies linearly with sqrt(c).

$$\boxed{\text{Lambda}_m = \text{Lambda}_m - A\ \text{sqrt}(c)}$$

<- A = constant
<- (solvent + temp)

Lambda_m got by EXTRAPOLATING to c -> 0.

Kohlrausch's Law

"Limiting molar conductivity is the sum of the contributions from individual ions."

$$\boxed{\text{Lambda}_m = v_+\ \text{lambda}_+ + v_-\ \text{lambda}}_-$$

<- v = stoichiometric coefficient of each ion

Use

Find Lambda for weak electrolytes indirectly.

$$\begin{aligned}\text{Lambda}_m(CH_3COOH) &\\ = \text{Lambda}_m(CH_3COONa) &\\ + \text{Lambda}_m(HCl) - \text{Lambda}_m(NaCl)&\end{aligned}$$

(combine strong-electrolyte data)

Weak Electrolytes : alpha & Ka

Weak electrolyte only partly dissociates :

$$HA \;\text{<=>}\; H^+ + A^-$$

Degree of dissociation

$$\boxed{\text{alpha} = \text{Lambda}_m \;/\; \text{Lambda}_m}$$ <- ratio of conductivities

alpha lies between 0 (no diss) and 1 (complete).

Ostwald's Dilution Law

	HA	<=>	H^+ +	A^-
initial	c		0	0
change	-c a		+c a	+c a
equm	c(1-a)		c a	c a

$$\boxed{K_a = c\,\text{alpha}^2 \;/\; (1 - \text{alpha})}$$ <- Ostwald's law

When alpha << 1 : (1 - alpha) -> 1, so

$$\boxed{K_a \quad c\,\text{alpha}^2 \;;\quad \text{alpha} = \text{sqrt}(K_a/c)}$$

Smaller c => larger alpha (dilution shifts forward).

Worked Example 4

For 0.001 M CH_3COOH at 298 K :

Lambda$_m$ = 49.9 ; Lambda$_m$ = 390.5 S cm^2 mol^{-1} .

Find alpha and Ka.

Step 1 : degree of dissociation

$$\text{alpha} = \text{Lambda}_m \,/\, \text{Lambda}_m = 49.9 \,/\, 390.5$$
$$= 0.128$$

$$\boxed{\text{alpha} = 0.128}$$

Step 2 : apply Ostwald

$$K_a = c\ \text{alpha}^2 \,/\, (1 - \text{alpha})$$
$$= (0.001)(0.128)^2 \,/\, (1 - 0.128)$$
$$= (0.001)(0.01638) \,/\, 0.872$$
$$= 1.638 \times 10^{-5} \,/\, 0.872$$

$$\boxed{K_a = 1.88 \times 10^{-5}}$$ <- weak acid - matches lit.

pKa = - log Ka = 4.73 .

Note : at higher c, alpha drops -> Ka stays constant.

Faraday's Laws of Electrolysis

1st Law

"Mass deposited or liberated at an electrode is directly proportional to the quantity of charge passed."

m proportional to $Q = I\,t$

$$\boxed{m = Z\,I\,t = (M\,I\,t) / (n\,F)}$$

<- $Z = M/(nF)$ = electrochemical equivalent

Faraday Constant

$$\boxed{F = N_A \times e = 96\,500 \text{ C / mol}}$$

<- charge on 1 mole of electrons

Symbols

① m = mass deposited (g)
② M = molar mass (g/mol)
③ n = electrons per ion (eg Cu^{2+} -> $n=2$)
④ I = current (A)
⑤ t = time (s)
⑥ $Q = I\,t$ = total charge (C)

Faraday's 2nd Law

"When the same quantity of electricity is passed through different electrolytes connected in series, the masses deposited are proportional to their equivalent masses."

$$\boxed{m_1 / m_2 = E_1 / E_2}$$

<- $E = M / n$ (equivalent mass)

Quick check

Pass same Q through $AgNO3$ and $CuSO4$ solns :

$$m_{Ag} / m_{Cu} = E_{Ag} / E_{Cu} ..$$
$$= (108/1) / (63.5/2)$$
$$= 108 / 31.75 = 3.40$$

So 3.40 g of Ag deposit for every 1 g of Cu.

Industrial use

Used in : electroplating (Ag, Au, Cr, Ni)
electro-refining of Cu and Al
extraction of Na, K, Al by electrolysis
electrolysis of brine (Cl2 + NaOH)

Worked Example 5

A current of $I = 1.5$ A is passed through $CuSO_4$ solution for $t = 10$ min. How much copper is deposited on the cathode?

Given : $M(Cu) = 63.5$ g/mol , $n = 2$,
$F = 96500$ C/mol .

Step 1 : charge passed

$$Q = I t = 1.5 \times (10 \times 60)$$
$$= 1.5 \times 600 = 900 \text{ C}$$

Step 2 : apply Faraday's 1st law

$$m = (M Q) / (n F)$$
$$= (63.5 \times 900) / (2 \times 96500)$$
$$= 57150 / 193000$$

$$\boxed{m = 0.296 \text{ g of Cu}}$$ <- approx 0.3 g

Check : moles Cu = m/M = 0.296/63.5 = 4.66e-3 ;
electrons needed = 2 x 4.66e-3 = 9.33e-3 mol OK.

Worked Example 6 (Ag plating)

How long must a current of $I = 0.50$ A pass through $AgNO_3$ to deposit $m = 10$ g of Ag ?

Given : $M(Ag) = 108$ g/mol , $n = 1$,
$F = 96500$ C/mol .

Step 1 : charge needed

$$Q = (m \times n \times F) / M$$
$$= (10 \times 1 \times 96500) / 108$$
$$= 965000 / 108$$

$$\boxed{Q = 8935\ \text{C} . \qquad 8.94 \times 10^3\ \text{C}}$$

Step 2 : time from $Q = I t$

$$t = Q / I = 8935 / 0.50$$
$$= 17\,870\ \text{s}$$
$$= 17870 / 60 = \text{~~149 min~~} \quad 298\ \text{min}$$

$$\boxed{t = 298\ \text{min} \qquad 4\ \text{hr}\ 58\ \text{min}}$$

<- CORRECTED
<- answer ?

Batteries (Galvanic Cell Types)

Primary cells

Reaction occurs only ONCE - cannot be recharged.

Once reactants used up, cell is dead.

① Dry cell (Leclanche) - Zn / MnO_2

anode : Zn can ; cathode : graphite rod ;

electrolyte : paste of NH_4Cl + $ZnCl_2$; EMF 1.5 V.

② Mercury cell - $Zn(Hg)$ / HgO

EMF = 1.35 V , constant during life (watches).

Secondary cells

Can be RECHARGED by reversing the current.

Reversible chemical reaction.

① Lead-acid - 2.04 V per cell (car)

② Nickel-Cadmium - 1.25 V (longer life)

Fuel cells

Continuously supplied fuel (H_2, CH_3OH) +

oxidiser (O_2). Convert chemical -> electrical

directly without combustion.

Used in Apollo space missions ; pollution-free.

Lead-Acid Storage Battery

Construction

Anode : spongy lead (Pb)

Cathode : PbO_2 (grid)

Electrolyte : 38% H_2SO_4 (aq) , density 1.25

Discharge reactions

Anode : $Pb + SO_4^{2-} \rightarrow PbSO_4 + 2e^-$

Cath : $PbO_2 + SO_4^{2-} + 4H^+ + 2e^-$
$\rightarrow PbSO_4 + 2H_2O$

$$\boxed{Pb + PbO_2 + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O}$$

<- OVERALL DISCHARGE

$$\boxed{\text{EMF per cell} = 2.041\ V}$$

<- car battery
<- 6 cells => 12 V

Charging

Reverse current => discharge reaction is reversed :

$$2PbSO_4 + 2H_2O \rightarrow Pb + PbO_2 + 2H_2SO_4$$

Density of H2SO4 rises again (1.25 -> 1.30) - way to check state of charge.

H2 - O2 Fuel Cell

Construction

Two porous carbon electrodes containing Pt or Pd catalyst ; electrolyte = aqueous KOH. H2 bubbled at anode, O2 at cathode.

Electrode reactions

Anode : $2\ H_2 + 4\ OH^- \rightarrow 4\ H_2O + 4e^-$

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

$$\boxed{2\ H_2 + O_2 \rightarrow 2\ H_2O}$$ <- overall

$$\boxed{E^{o}_{cell} = +1.23\ V}$$ <- (standard)

Advantages

① High efficiency (70% vs 40% IC engine)

② No pollution - product is only water

③ Continuous power - fuel supplied externally

④ Quiet operation (no moving parts)

Used in : Apollo space missions (also drinking water for astronauts), modern H2 cars.

Corrosion / Rusting of Iron

Corrosion = unwanted electrochemical oxidation of a metal by surroundings.

Iron in moist air forms a tiny galvanic cell on the surface (water droplet = electrolyte) :

Mechanism

Anode : $Fe \rightarrow Fe^{2+} + 2e^-$

Cath : $4 H^+ + O_2 + 4e^- \rightarrow 2 H_2O$

$Fe^{2+} + (O_2 , H_2O) \rightarrow Fe_2O_3 \times H_2O$

(rust - hydrated iron(III) oxide)

E^0_{cell}	+ 1.67 V	(very spontaneous)

Conditions needed

① Water (moisture)
② Oxygen (air)
③ Electrolyte (H+) - acidic rain ; salt

Prevention

a) Barrier coating : paint, oil, plastic

b) Galvanisation : coat with Zn (sacrificial anode)

c) Cathodic protection : connect to Mg / Zn block

Summary Card - Key Formulas

① Cell EMF

$$\boxed{E^0_{cell} = E^0_{cath} - E^0_{anode}}$$

② Gibbs energy

$$\boxed{dG^0 = - n F E^0_{cell}}$$

③ Equilibrium K

$$\boxed{\log K = n E^0_{cell} / 0.0591}$$

④ Nernst (298 K)

$$\boxed{E_{cell} = E^0_{cell} - (0.0591/n) \log Q}$$

⑤ Conductivity

$$\boxed{\text{kappa} = G\ (L/A)\ ;\ \text{unit}\ S\ cm^{-1}}$$

⑥ Molar conductivity

$$\boxed{\text{Lambda}_m = \text{kappa} \times 1000 / c}$$

⑦ Faraday's 1st law

$$\boxed{m = (M I t) / (n F)}$$

⑧ Pb-acid EMF & fuel cell

Pb-acid : 2.04 V/cell ; H_2-O_2 fuel : 1.23 V

F = 96500 C/mol , R = 8.314 J K-1 mol-1 , T = 298 K