Ion mobility

Qualitatively: Large ions in viscous liquids can be expected to be drifting slowly and have low conductivities

Quantitatively: drift velocity $s = uE$

electric field strength

ion mobility

Two forces are acting on the ion: $F_{field} = zeE$

elementary charge

number of ion charges

Stokes' law $F_{retardation} = 6\pi\eta rs$

drift velocity

ion radius

viscosity

When the ion has reached its drift velocity, both forces are equal!

$$\Rightarrow \quad ezE = 6\pi\eta rs \quad \Rightarrow \quad s = \frac{ezE}{6\pi\eta r}$$

u

$$u = \frac{s}{E} = \frac{ez}{6\pi\eta r} \qquad [m^2 s^{-1} V^{-1}]$$

ionic conductivities:

$\lambda_+ = z_+ F u_+ \qquad \lambda_- = z_- F u_-$

Faraday constant

Measured ion mobilities

$$u = \frac{ez}{6\pi\eta r}$$

⇒ **u is high for an ion that is:**

- **highly charged**
- **in a solution of low viscosity**
- **of small radius r**

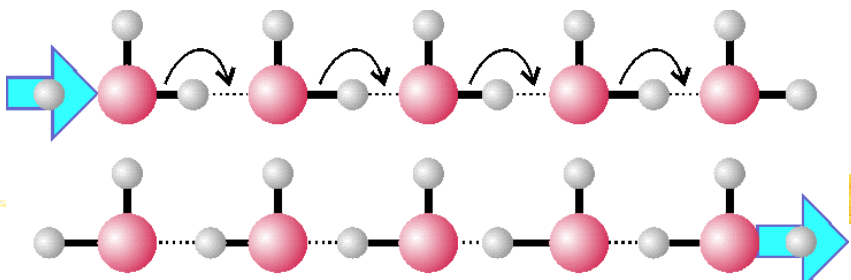
BUT: r = hydrodynamic radius (including water ligands)

Table 9.2 *Ionic mobilities in water at 298 K, $u/(10^{-8}\ m^2\ s^{-1}\ V^{-1})$*

Cations		Anions	
H^+	36.23	OH^-	20.64
Li^+	4.01	F^-	5.74
Na^+	5.19	Cl^-	7.92
K^+	7.62	Br^-	8.09
Rb^+	8.06	I^-	7.96
Cs^+	8.00	CO_3^{2-}	7.18
Mg^{2+}	5.50	NO_3^-	7.41
Ca^{2+}	6.17	SO_4^{2-}	8.29
Sr^{2+}	6.16		
NH_4^+	7.62		
$[N(CH_3)_4]^+$	4.65		
$[N(C_2H_5)_4]^+$	3.38		

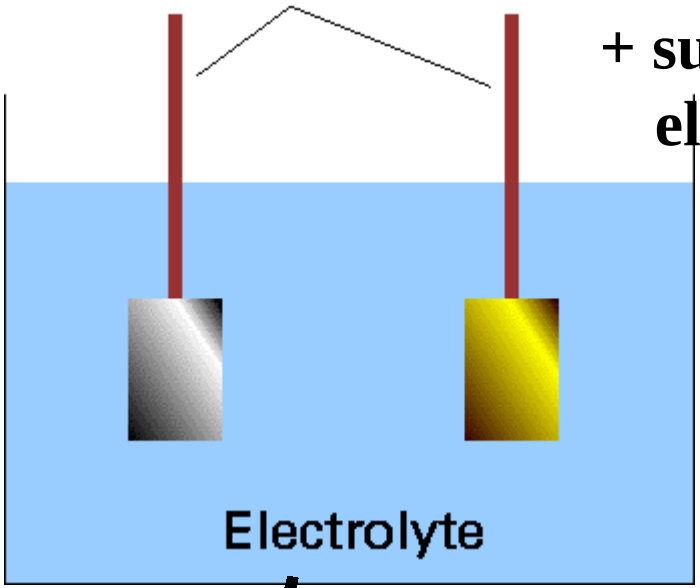
BUT

Special case H^+: Grotthus conduction mechanism



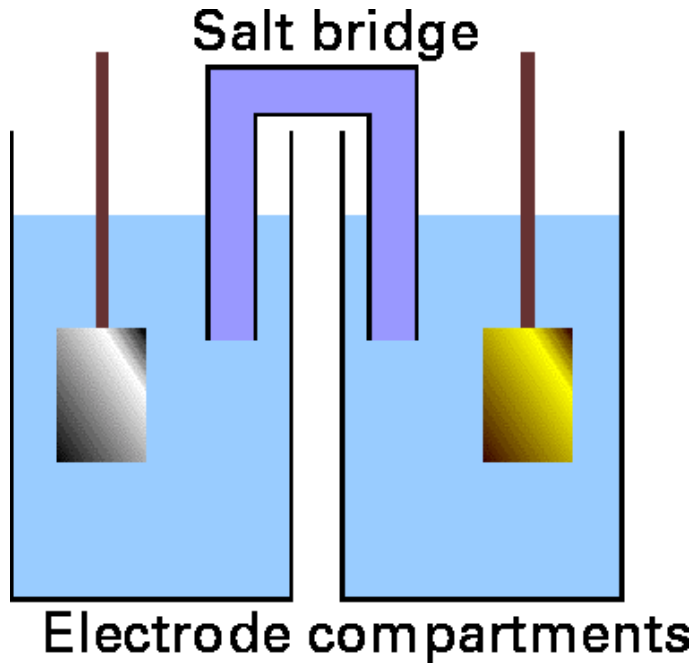
Electrochemical cells

Electrodes = electronic conductor + surrounding electrolyte



electrode compartment

If two different electrolytes are used:

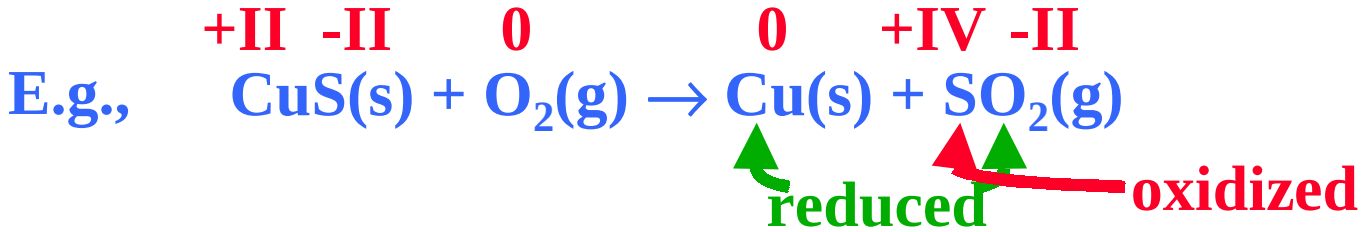


Galvanic cell: electrochemical cell in which electricity is produced as a result of a spontaneous reaction (e.g., fuel cells, electric fish!)

Electrolytic cell: electrochemical cell in which a non-spontaneous reaction is driven by an external source of current

Reactions at electrodes: Half-reactions

Redox reactions: Reactions in which electrons are transferred from one species to another



Any redox reactions can be expressed as the difference between two reduction half-reactions in which e^- are taken up

Reduction of Cu^{2+}: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

Reduction of Zn^{2+}: $Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$

Difference: $Cu^{2+}(aq) + Zn(s) \rightarrow Cu(s) + Zn^{2+}(aq)$

More complex: $MnO_4^-(aq) + 8H^+ + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$

Half-reactions are only a formal way of writing a redox reaction

Carrying the concept further

Reduction of Cu^{2+}: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

In general: redox couple Ox/Red, half-reaction $Ox + \nu e^- \rightarrow Red$

Any reaction can be expressed in redox half-reactions:

$2\ H^+(aq) + 2e^- \rightarrow H_2(g, p_f)$

$2\ H^+(aq) + 2e^- \rightarrow H_2(g, p_i)$

Expansion of gas: $H_2(g, p_i) \rightarrow H_2(g, p_f)$

$AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)$

$Ag^+(aq) + e^- \rightarrow Ag(s)$

Dissolution of a sparingly soluble salt: $AgCl(s) \rightarrow Ag^+(aq) + Cl^-(aq)$

Reaction quotients: $Q = a_{Cl^-} \approx [Cl^-]$ $\quad Q = \frac{1}{a_{Ag^+}} \approx \frac{1}{[Ag^+]}$