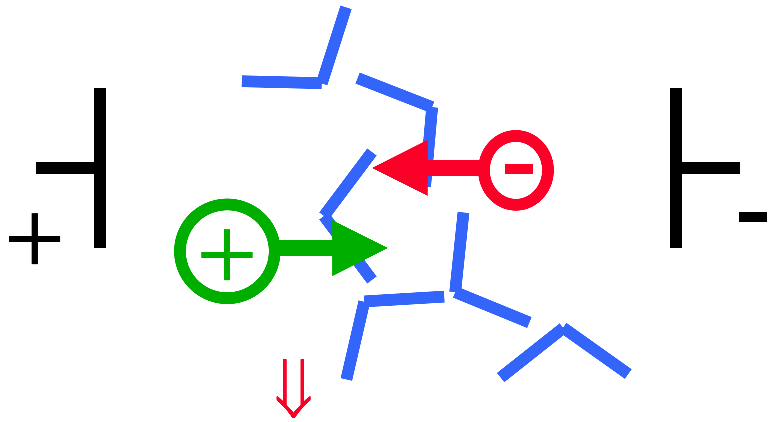
Chemistry involving ions: Electrochemistry

Atkins, Chapter 9

Ions migrate in electric fields



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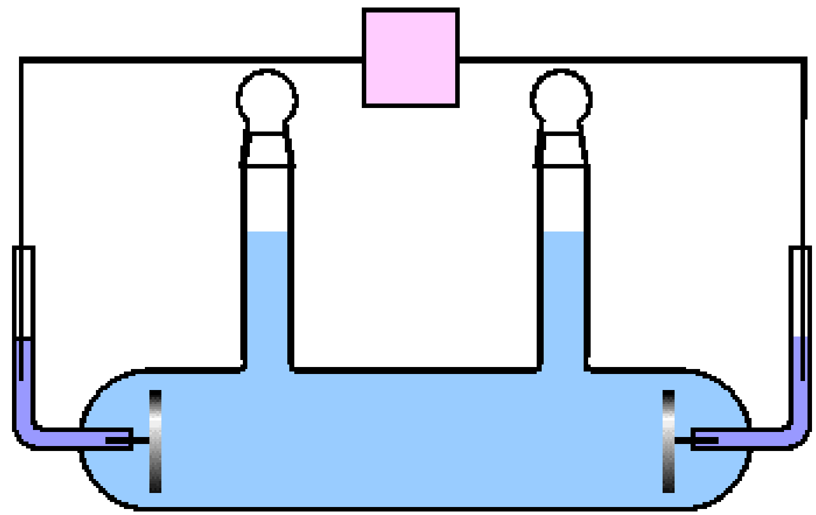
a current flows

Conductivity bridge



resistivity

potential difference

length of sample

resistance $R = \frac{V}{I} = \frac{\rho l}{A} \quad [\Omega]$

current

cross-sectional area

conductivity $\kappa = \frac{1}{\rho} \quad [\Omega^{-1} m^{-1} = S m^{-1}]$

siemens

molar conductivity:

$$\Lambda_m = \frac{\kappa}{c} \quad [S m^2 mol^{-1}]$$

Ionic conductivities

The molar conductivity varies with concentration (ions influence each other)

For a strong electrolyte (complete dissociation) [Kohlrausch (1876)]:

$$\Lambda_m = \Lambda_m^{o} - K\sqrt{c}$$

Constant to take ion-ion interactions into account

Limiting molar conductivity (c → 0 M)

$$\Lambda_m^{o} = \lambda_{+} + \lambda_{-}$$

ionic conductivities = contributions of cation and anion species

Table 9.1 *Ionic conductivities, $\lambda/(\mathrm{mS\ m^2\ mol^{-1}})$**

Cations		Anions	
$H^+(H_3O^+)$	34.96	OH^-	19.91
Li^+	3.87	F^-	5.54
Na^+	5.01	Cl^-	7.64
K^+	7.35	Br^-	7.81
Rb^+	7.78	I^-	7.68
Cs^+	7.72	CO_3^{2-}	13.86
Mg^{2+}	10.60	NO_3^-	7.15
Ca^{2+}	11.90	SO_4^{2-}	16.00
Sr^{2+}	11.89	$CH_3CO_2^-$	4.09
NH_4^+	7.35	HCO_2^-	5.46
$[N(CH_3)_4]^+$	4.49		
$[N(C_2H_5)_4]^+$	3.26		

*The same numerical values apply when we select the units $\mathrm{S\ m^{-1}\ (mol\ L^{-1})^{-1}}$.

Ion mobility

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

Quantitatively: **drift velocity** $s = uE$

- E: **electric field strength**
- u: **ion mobility**

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

- E: electric field strength
- e: **elementary charge**
- z: **number of ion charges**

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

- s: **drift velocity**
- r: **ion radius**
- η: **viscosity**

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

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

where $\frac{ez}{6\pi\eta r}$ is u:

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

ionic conductivities:

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

F: **Faraday constant**

Measured ion mobilities

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

$\Rightarrow$ 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)

BUT

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		

Special case H^+: Grotthus conduction mechanism