Homogeneous electrochemistry

Electric current and current density

Electrical conduction: a transport phenomenon in which electrical charge (carried by electrons or ions) moves through the system.

The **electric current** (I) is defined as the rate of flow of charge through the conducting material:
$$I=dQ/dt$$
where dQ is the charge that passes through a cross section of the conductor in time dt.

The **electric current density** j is the electric current per unit cross-sectional area:
$$j=I/A$$
where A is the conductor's cross-sectional area.

Ampere, elementary charge, Faraday constant

The **SI unit of electric current** is the **ampere** (A) and equals one coulomb per second:
$$1\ A = 1\ C/s$$

The charge Q is more fundamental than the current I, but it is easier to measure current than charge by measuring mechanical force.

The coulomb is defined as the charge transported in one second by a one-ampere current: $1\ C = 1\ A \cdot s$

The elementary charge is the **charge on the electron**,
$$e = -\ 1.602176634 \cdot 10^{-19}\ C.$$

The Faraday constant, $F = e \cdot N_A = 1.602176634 \cdot 10^{-19}\ C \cdot 6.02214076 \cdot 10^{23}\ mol^{-1}$
$\approx 96\ 485\ C\ mol^{-1}$

It shows the electric charge per one mol electron.

Michael Faraday
Born: 22 September 1791
Died: 25 August 1867
British physicist, chemist

Electric field and electric field strength

Electric field: a modell which describes the effect of a charge in distance

Electric field strength (E) is defined at a given point as the limit of the electrical force per unit charge on an infinitesimal test charge. $$E = \lim_{Q_t \to 0} F/Qt$$

The SI unit of the electric field strength is 1 N/C = 1 V/m.

Electric field strength of a point charge *Q* at a distance *r*

The magnitude of the force according the Coulomb's law $dF = \frac{|QdQ|}{4\pi\varepsilon_0 r^2}$

The **magnitude** of $E = \frac{dF}{dQ_t} = \frac{1}{4\pi\varepsilon_0 r^2}|Q|$

The **direction**: the small probe charge is positive, therefore for positive *Q* charge *E* directs outward, for negative *Q* charge it directs inward.

Electric potential

Electric potential (ϕ): an alternative description instead of the electric field

Electric potential difference ($\phi_b - \phi_a$) is the work per unit charge to move a test charge reversible from *a* to *b*.

$$\varphi_b - \varphi_a = dw_{ab}/Q_t$$

Usual convention to choose point *a* at infinity (where the test charge interacts with no other charges) and to define ϕ at infinity as zero.

$$\varphi_b = dw_{\infty b}/Q_t$$

The SI unit of the electric potential is volt (V): 1 V = 1 J/C

The electric field strength can be expressed by the electric porential as its spatial gradient:
$$E = \text{grad}\phi$$
(grad vector is formed from the spatial derivatives for each coordinate)

Features of the electric potential

- ϕ increases as one moves closer to a positive charge.

- A negative charge moves spontaneously toward a positive charge, so *electrons move spontaneously from regions of low to regions of high electric potential within a phase.*

- Electric fields and electric potentials are defined at a "point" in matter, but we generally mean the average field and the average potential in a very small volume containing which is much larger than atoms. (Note: The electric field within a single molecule shows very sharp variations.)

- In thermodynamic equilibrium there are no current flows, therefore the electric force is zero, the electric potential is the same in all points of the phase. If the phase has a net charge it is repulsed to the surface of the phase.
Electroneutrality: in the inner space of a conductive phase the net charge is zero.

Consequence of charge on surface

What if there is some charge on the surface of a conductive phase?

Let us take a silver sphere having 1 mol Ag atoms! M_{Ag} = 107.8682 g/mol, $\rho_{Ag,20°C}$ = 10,50 g/cm³,

therefore its radius: $r = \sqrt[3]{\dfrac{3}{4\pi}\dfrac{M_{Ag}}{\rho_{Ag,20°C}}} = 1.348$ cm

Let it be only 10^{-12} mol Ag$^+$ ion on its surface (charges are repulsed to the surface) in vacuum and calculate its electric potential:

$$\varphi = \frac{1}{4\pi\varepsilon_r\varepsilon_0}\frac{Q}{r} = \frac{1}{4\pi \cdot 1 \cdot 8.854187 \cdot 10^{-12}\frac{As}{Vm}}\frac{96485\frac{C}{mol} \cdot 10^{-12}\text{ mol}}{0.01348 \text{ m}} = 6.433 \cdot 10^4 \text{ V}$$

Very high potential, but 10^{-12} mol Ag$^+$ ion chemically undetectable!

The chemical compostion of the phese are the same, but their electric potential is different!

Charge number, electrochemical system

Charge number (z_i): the charge of one particle of species *i* is proportional to the elementary charge, the proportionality factor is the charge number.

> e.g. for Zn^{2+} $z_i = 2$, for H_2O $z_i = 0$, for Cl^- $z_i = -1$

Electrochemical system: systems having condensed phase in which at least in one phase ions can move due to the potential gradient (electric field).

Can be **homogeneous** (e.g. melted salts) or **heterogeneous** (e.g. electrolyte solution and metal).

In an electrochemical system the phases have different electric potentials.

The electric potential difference $\Delta\phi$ can not be measure directly.

$\Delta\phi$ comes mainly from charge transferred between phases. The amount of material caused this is far too small to be chemically detected.

Activities

Not very diluted solutions bahaves a bit different compared to the ideal one. Some laws become less accurate and the inaccuracy grows as they become more and more concentrated.

Reason: The interaction between the solute particles which is negligible in very diluted solutions becomes significant.

We can take this interaction into account if we introduce the activity and the activity coefficient.

One can say that activity is a kind of effective concentration what is easy to imagine. The solution behaves more or less concentrated than it is.
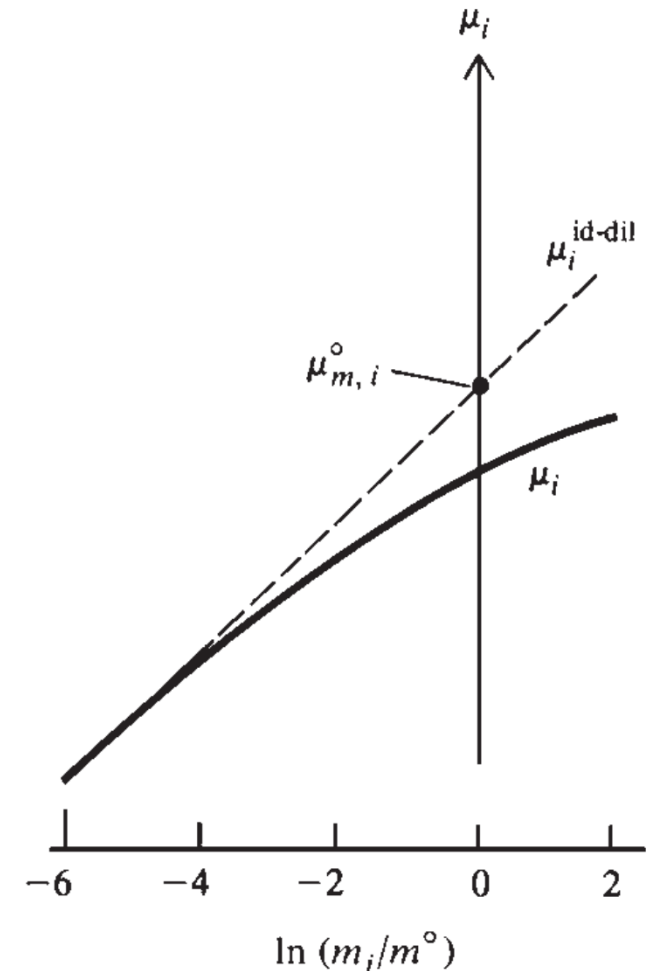
Levine: Physical Chemistry 6th Edition
Fig. 10.5

Activity coefficient

Reminder TT lecture 5 p16

Chemical potential in ideal mixtures: $\mu_i^{\text{ideal}} = \mu_i^\circ + RT\ln x_i$

Chemical potential in real mixtures: $\mu_i = \mu_i^\circ + RT\ln a_i$

The difference of these equations measures the **nonideality** of the mixture, therefore:
$$\mu_i - \mu_i^{\text{ideal}} = RT\ln a_i - RT\ln x_i = RT\ln(a_i/x_i)$$

Let us introduce the activity coefficient, $\gamma_i = \dfrac{a_i}{x_i}$ which measures the degree of the deviation from the ideal diluted behaviour.

Activity coefficients

Activity can be written similarly using molality or molar concentration.

$$\gamma_{m,i} = \frac{a_i m^\circ}{m_i}, \text{ where } m^\circ = 1 \text{ mol/kg}$$

$$\gamma_{c,i} = \frac{a_i c^\circ}{c_i}, \text{ where } c^\circ = 1 \text{ mol/dm}^3$$

It leads to $\mu_i = \mu_i^\circ + RT\ln(m_i\gamma_i/m^\circ)$ and $\mu_i = \mu_i^\circ + RT\ln(c_i\gamma_i/c^\circ)$.

If we dilute a solution its behaviour closes to the ideal one, therefore any type of activity coefficient closes to 1 ($\gamma_i \rightarrow 1$).

Activity and activity coefficients have no unit.

The activity coefficient value depends on the concentration units used.

Electrolytes

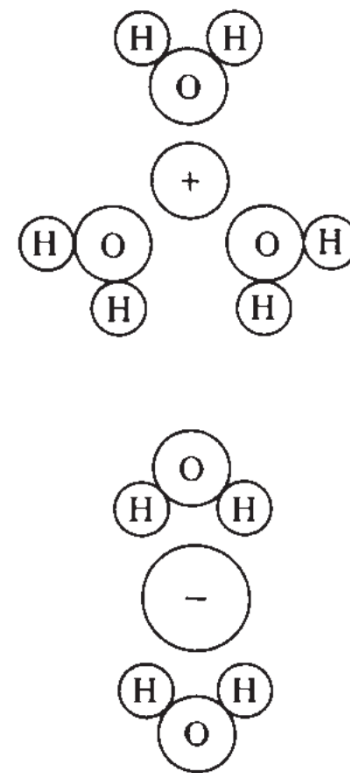An **electrolyte** is a substance that yields ions in solution.

Weak or strong electrolites: provides small amont of ions or very much.

Solvatation: the ions are surraunded by a shealth of a few solvent molecules bound to the ion by electrostatic forces and traveling through the solution with the ion.
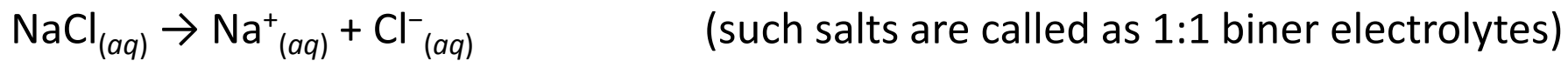
Hydration: solvatation in water.

Due to the numerous charged ions usage of activities is essential.

Electrolyte solutions reach ideal dilution at far less concentration than nonelectrolite solutions.

Levine: Physical Chemistry 6th Edition
Fig. 10.7

Chemical Potentials in Electrolyte Solutions

$NaCl_{(aq)} \rightarrow Na^+_{(aq)} + Cl^-_{(aq)}$ (such salts are called as 1:1 biner electrolytes)

The chemical potential of the salt is the sum of that of the ions:

$$\mu_{NaCl,aq} = \mu_{Na^+,aq} + \mu_{Cl^-,aq} = \mu^\circ_{Na^+,aq} + RT\ln a_{Na^+,aq} + \mu^\circ_{Cl^-,aq} + RT\ln a_{Cl^-,aq}$$

Using a simplified notation:

$$\mu_{salt} = \mu_+ + \mu_- = \mu^\circ_+ + RT\ln a_+ + \mu^\circ_- + RT\ln a_- = \mu^\circ_{salt} + RT\ln(a_+ a_-)$$

μ_+ or μ_- can not be measured induvidually (nobody can change the number of cations and anions independently), just μ_{salt}

$a_+ a_-$ product is called as activity of the salt, $a_{salt} = a_+ a_-$

These equations are valid for any 1:1 biner electrolytes.

Chemical Potentials in Electrolyte Solutions

Introducing the activity coefficients: $a_{\text{salt}} = a_+ a_- = \dfrac{m_+ \gamma_+ m_- \gamma_-}{m^{\circ 2}}$

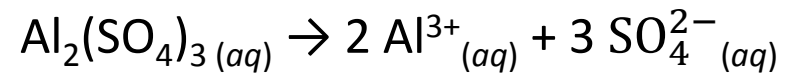For a 1:1 salt the molality of salts equals to the molality of ions: $m = m_+ = m_-$

Let us introduce the **mean activity coefficient,** $\gamma_\pm = (\gamma_+ \gamma_-)^{1/2}$

$$a_{\text{salt}} = \frac{m^2}{m^{\circ 2}} \gamma_\pm^2$$

$$\mu_{\text{salt}} = \mu_{\text{salt}}^\circ + RT\ln\left(\frac{m^2}{m^{\circ 2}} \gamma_\pm\right)$$

In general the **mean activity coefficient**: $\gamma_\pm = (\gamma_+{}^{\nu_+} \gamma_-{}^{\nu_-})^{\frac{1}{\nu_+ + \nu_-}}$
(This is the geometric mean of the activity coefficients.)

$$a_{\text{salt}} = \left(\frac{m_+}{m^\circ}\right)^{\nu_+} \left(\frac{m_-}{m^\circ}\right)^{\nu_-} \gamma_\pm^{\nu_+ + \nu_-}$$

Chemical Potentials in Electrolyte Solutions

$$Al_2(SO_4)_{3\,(aq)} \rightarrow 2\,Al^{3+}_{(aq)} + 3\,SO_4^{2-}{}_{(aq)}$$

The chemical potential of the salt is the sum of that of the ions:

$$\mu_{Al_2(SO_4)_3,\mathrm{aq}} = 2\mu_{Al^{3+},\mathrm{aq}} + 3\mu_{SO_4^{2-},\mathrm{aq}}$$

$$= 2\mu^{\circ}_{Al^{3+},\mathrm{aq}} + 2RT\ln a_{Al^{3+},\mathrm{aq}} + 3\mu^{\circ}_{SO_4^{2-},\mathrm{aq}} + 3RT\ln a_{SO_4^{2-},\mathrm{aq}}$$

The activity of the salt:

$$a_{\mathrm{salt}} = \left(\frac{m_+}{m^{\circ}}\right)^{\nu_+} \cdot \left(\frac{m_-}{m^{\circ}}\right)^{\nu_-} \cdot \gamma_{\pm}^{\nu_+ + \nu_-} = \left(\frac{2m}{m^{\circ}}\right)^2 \left(\frac{3m}{m^{\circ}}\right)^3 \cdot \gamma_{\pm}^{2+3} = \gamma_{\pm}^5 \cdot 108 \left(\frac{m}{m^{\circ}}\right)^5$$

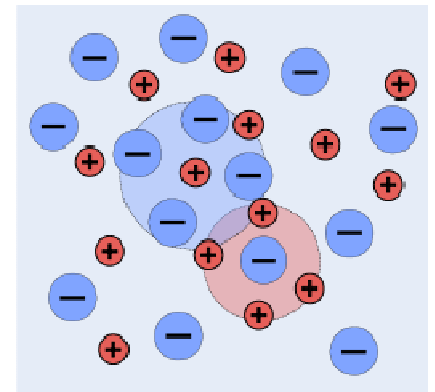# Calculation of the mean activity coefficient
The effect of the ionic atmosphere

Reason of activity: interaction between the solute particles.

Due to it the **motion of ions** in solution is **not entirely random**.

Opposite charge ions to encounter each other more frequently than ions of the same charge. A time-averaged picture of the solution shows that **near any given ion, there is an excess of counter-ions.**

This time-averaged spherical distribution (in which ions of the same charge as the central ion and counter-ions are both present, though counter-ions predominate) has a net charge equal in magnitude but opposite in sign to the central ion, and is known as its **ionic atmosphere**.

Simple ionic atmosphere

Calculation of the mean activity coefficient
The Debye-Hückel Limiting Law

The Coulombic interaction stabilizes the ionic atmosphere and lowers the energy of the central ion.

Debye and Hückel assumed that the largest part of the interaction can be estimated using the **Coulombic interaction**.

Taking into account the Boltzmann distribution law of statistical mechanics, the basic equations of thermodynamics and electrostatics they derived a formula for the activity coefficients.

Erich Hückel
Born: 9 August 1896
Died: 16 February 1980
German physicist,
physical chemist
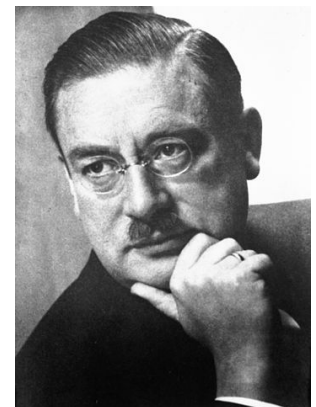
Peter Debye
Born: 24 March 1884
Died: 2 November 1966
Dutch physicist,
physical chemist

Calculation of the mean activity coefficient

The mean activity coefficient can be calculated using the Debye-Hückel equation (DH equation):

$$\ln\gamma_\pm = -z_+|z_-|\frac{AI^{1/2}}{1 + BaI^{1/2}}$$

where z_+, z_- are the charge numbers of the positive and negative ions, respectively; a is the diameter of uniformly charged hard spheres (ions), commonly interpreted as **mean ionic diameter**; A and B constants; and I is the **ionic strength**.

The **ionic strength** is defined as $I = \frac{1}{2}\sum_j z_j^2 m_j$
where z_j is the charge number and m_j is the molality of the jth ion.

In very dilute solutions I limits to zero, therefore the DH equation simplifies:

$$\ln\gamma_\pm = -z_+|z_-|AI^{1/2}$$

Validity of the Debye-Hückel Limiting Law

The assumptions made in the derivation of the law are valid only for very dilute solutions. Therefore increasing the ionic strength some deviation occurs from the predictions.

This plot shows the measured $\log_{10}\gamma_{\pm}$ (solid lines) versus the predictions of the Debye–Hückel limiting law (dotted lines).

The higher the ion charges are the lower the concentration at which the prediction is good up to.

At higher concentrations the DH equation can be modified empirically to make its predictions better.
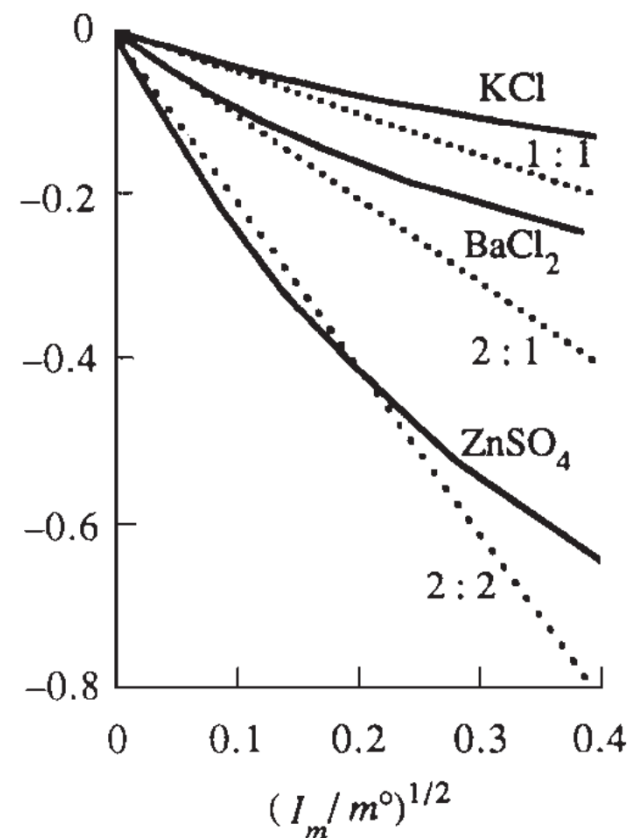
Levine: Physical Chemistry 6th Edition
Fig. 10.9

Sample calculations

Calculate the ionic strength of hydrochloric acid solution with molality 0.010 mol/kg!

$$I = \tfrac{1}{2} \sum_j z_j^2 m_j$$

$m_{H^+} = m_{Cl^-} = 0.010 \text{ mol/kg}$

$I = \tfrac{1}{2} \left(1^2 \cdot 0.010 \dfrac{\text{mol}}{\text{kg}} + (-1)^2 \cdot 0.010 \dfrac{\text{mol}}{\text{kg}} \right) = 0.010 \text{ mol/kg}$

Note: for a 1:1 biner electrolyte *I* gives the molality back.

Calculate the ionic strength of sodium sulphate solution with molality 0.014 mol/kg!

$m_{Na^+} = 0.028 \text{ mol/kg}$, $m_{SO_4^{2-}} = 0.010 \text{ mol/kg}$

$I = \tfrac{1}{2} \left(1^2 \cdot 0.028 \dfrac{\text{mol}}{\text{kg}} + (-2)^2 \cdot 0.010 \dfrac{\text{mol}}{\text{kg}} \right) = 0.034 \text{ mol/kg}$

Sample calculations

Calculate the ionic strength of a solution having 0.30 mol/kg KCl and 0.51 mol/kg $K_2Cr_2O_7$ dissolved!

$$I = \tfrac{1}{2} \sum_j z_j^2 m_j$$

$m_{Cl^-} = 0.30 \text{ mol/kg}, \ m_{Cr_2O_7^{2-}} = 0.51 \text{ mol/kg}, \ m_{K^+} = (0.30 + 2 \cdot 0.51)\frac{\text{mol}}{\text{kg}} = 1.32 \text{ mol/kg}$

$I = \tfrac{1}{2}\left(1^2 \cdot 1.32\frac{\text{mol}}{\text{kg}} + (-1)^2 \cdot 0.30\frac{\text{mol}}{\text{kg}} + (-2)^2 \cdot 0.51\frac{\text{mol}}{\text{kg}}\right) = 3.66 \text{ mol/kg}$

Sample calculations

Calculate the mean activity coefficient of a 0.00013 mol/kg solution of potassium phosphate! (The constant of the DH equation is $A = 0.511$ (mol/kg)$^{-0.5}$.)

$m_{K^+} = 3 \cdot 0.00013 \text{ mol/kg} = 0.00039 \text{ mol/kg}, z_{PO_4^{3-}} = 0.00013 \text{ mol/kg}$

$I = \frac{1}{2}\left(1^2 \cdot 0.00039 \frac{\text{mol}}{\text{kg}} + (-3)^2 \cdot 0.00013 \frac{\text{mol}}{\text{kg}} \right) = 0.00156 \text{ mol/kg}$

In very diluted solutions the DH equiation:

$\ln\gamma_{\pm} = -z_+|z_-|AI^{1/2} = -1 \cdot 3 \cdot 0.511 \left(\frac{\text{mol}}{\text{kg}} \right)^{-0.5} \cdot \left(0.00156 \frac{\text{mol}}{\text{kg}} \right)^{0.5} = -0.060549$

Therefore $\gamma_{\pm} = e^{-0.060549} = 0.941$

The electrochemical potential

Reminder Chemical potential (TT lecture 5 p11) for species i in phase α:

$$\mu_i^\alpha = \left(\frac{\partial G^\alpha}{\partial n_i^\alpha}\right)_{p,T,n_j}$$

The **electrochemical potential** of species i is the sum of the chemical potential and the molar electrostatic potential energy $\tilde{\mu}_i^\alpha = \mu_i^\alpha + z_i F \varphi^\alpha$

For neutral species $\tilde{\mu}_i^\alpha = \mu_i^\alpha$.

For charged cpecies the electrochemical potential replaces the chemical potential in all thermodynamic equations.

The separation of the chemical and the electric part is only a modell, there is no materialless charge!

The electrical charge transport

Electrical conduction: a transport phenomenon in which electrical charge (carried by electrons or ions) moves through the system.

Reminder TT lecture 8 Transport

12 slides about different phenomena, but do you know what transport is in general?

The transport

Due to the spatial inhomogenity of an intensive variable matter and energy is moving causing the change of extensive variables.

„the main discovery of Onsager: transport of an extensive property is proportional to the gradient of the corresponding intensive quantity" TT lecture 8 p11

Due to the concentration inhomogenity species transport occurs.
Due to the temperature inhomoganity energy (heat) transport occurs.
Due to flow velocity inhomogenity translational momentum transport occurs.

Very similar phenomena, and similar laws!

The balance equation

An extensive quantity can change:
- **by transport (displacement of energy and matter cause the change)**
- by source (the change occurs without displacement, e.g. a species is produced in a chemical reaction)

We can write a differential equation (balance equation) for the change of quantity Y_i:

$$\frac{dY_i}{dt} = Si - \frac{dF_i}{dx}$$

change in time = production/consumption − export/import

where Y_i can be any extensive quantity, S_i is the source/sink of it, F_i is the flux of the quantity.

Flux: the displace amount of quantity per unit time and through unit area.

The general transport equation

If we do not have convention the **flux is proportional to the gradient of a driving force**:

$$J_i = Li \cdot \mathrm{grad}Z$$

where L_i is the conductivity coefficient.

phenomenon	flux	driving force	coefficient	describing law
viscosity	impulse perpendicular the flow $\dfrac{1}{A}\dfrac{d(mv_x)}{dt}$	speed gradient $\dfrac{dv_x}{dy}$	viscosity coefficient, η	Newton's Second Law $\dfrac{1}{A}\dfrac{dmv_x}{dt} = -\eta\dfrac{dv_x}{dy}$ more known form: $F = -\eta A\dfrac{dv_x}{dy}$
diffusion	chemical matter $\dfrac{1}{A}\dfrac{dn}{dt}$	concentration gradient $\dfrac{dc}{dx}$	diffusion coefficient, D	Fick's first law $\dfrac{1}{A}\dfrac{dn}{dt} = -\mathrm{D}\dfrac{dc}{dx}$
heat	heat energy $\dfrac{1}{A}\dfrac{dq}{dt}$	temperature gradient $\dfrac{dT}{dx}$	thermal conductivity coefficient, λ	Fourier's law $\dfrac{dT}{dx} = -\lambda\dfrac{1}{A}\dfrac{dq}{dt}$

The general transport equation

phenomenon	flux	driving force	coefficient	describing law
viscosity	impulse perpendicular the flow $$\frac{1}{A}\frac{d(mv_x)}{dt}$$	speed gradient $$\frac{dv_x}{dy}$$	viscosity coefficient, η	Newton's Second Law $$\frac{1}{A}\frac{dmv_x}{dt} = -\eta\frac{dv_x}{dy}$$ more known form: $$F = -\eta A\frac{dv_x}{dy}$$
diffusion	chemical matter $$\frac{1}{A}\frac{dn}{dt}$$	concentration gradient $$\frac{dc}{dx}$$	diffusion coefficient, D	Fick's first law $$\frac{1}{A}\frac{dn}{dt} = -\mathrm{D}\frac{dc}{dx}$$
heat conductivity	heat energy $$\frac{1}{A}\frac{dq}{dt}$$	temperature gradient $$\frac{dT}{dx}$$	thermal conductivity coefficient, λ	Fourier's law $$\frac{dT}{dx} = -\lambda\frac{1}{A}\frac{dq}{dt}$$
electric conductivity	electric charge $$\frac{1}{A}\frac{dQ}{dt}$$	potential gradient $$\frac{d\varphi}{dx}$$	conductivity (formerly specific conductance), κ	Ohm's law $$\frac{1}{A}\frac{dQ}{dt} = -\kappa\frac{d\varphi}{dx}$$ more known forms: $$\mathrm{I} = \frac{U}{R} \text{ and } j = \kappa \cdot E$$

The cross effects

Not only diagonal, but offdiagonal effects exist!

	speed gradient	concentration gradient	temperature gradient	potential gradient
impulse perpendicular the flow	viscosity			
chemical matter		diffusion	thermodiffusion or Soret effect	ion migration, electrophoresis
heat energy			heat conductivity	Peltier effect
electric charge		charge transport by the diffusion of ions	Seebeck effect (thermocouples)	electric conductivity

Conductivity

Conductivity (κ): the coefficient of electric conductivity.

SI unit: $\dfrac{1}{\Omega\text{m}} = \dfrac{\text{S}}{\text{m}}$ S unit is Siemens

Conductivity of water is somehow proportional to the ioninc content, therefore measung the conductivity one can monitor water purity and water quality.

Name	κ / µS cm^{-1}
teflon	~10^{-20} µS/cm
dry wood	~10^{-11} µS/cm
glass	~10^{-9} µS/cm
wet wood	~1 µS/cm
absolute pure water	0.055 µS/cm
power plant boiler water	1 µS/cm
good city water	50 µS/cm
ocean water	53µS/cm
31% HNO$_3$ solution	865 µS/cm
silicon	15.6 µS/cm
germanium	$2.17 \cdot 10^4$ µS/cm
iron	$1.04 \cdot 10^{11}$ µS/cm
copper	$5.98 \cdot 10^{11}$ µS/cm
silver	$6.30 \cdot 10^{11}$ µS/cm

Specific resistivity and conductance

Specific resistivity (ρ): $\rho = \dfrac{1}{\kappa}$ SI unit: $\Omega \cdot \text{m}$
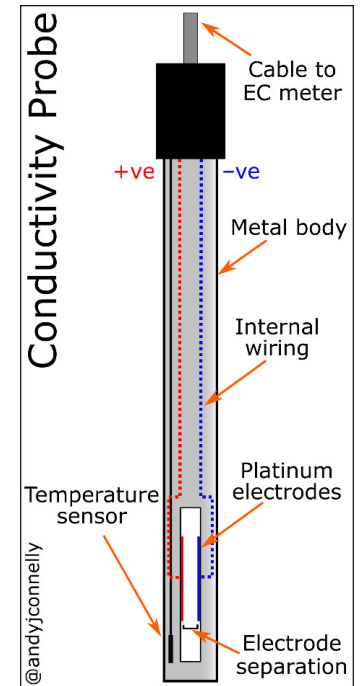
Resistance of a homogeneous uniform wire: $R = \rho \dfrac{l}{A}$ SI unit: Ω

where l is the length of wire, A is the cross sectional area of wire

Conductance: $G = \dfrac{1}{R}$ SI unit: $\Omega^{-1} = \text{S}$

How to measure conductance, conductivity?

Technically: use a **conductometer (also called conductivity meter)**!

How to measure conductance, conductivity?

Background of the measurement

special electronic device

- applies high frquency AC voltage which cause very small electric current and polarization
- measures the response of the electrodes (impedance)

conductivity probe

- forms an electrochemical cell with the solution
- contains two noble metal electrodes
- open to the liquid, but typically covered by a protective shell

The electric circuit of the conductivity meter

Let us give the current using Ohm's law!

Through the conductivity cell: $I = \dfrac{U}{R_c + R_m}$

Through the measuring resistance: $I = \dfrac{U_m}{R_m}$

The same current flows, so these are equal
to each other: $\dfrac{U}{R_c + R_m} = \dfrac{U_m}{R_m}$

conductivity cell

AC signal electric power source

voltage dropping on R_m measuring resistance

Select R_m to be much less than R_c, so $R_c + R_m \approx R_c$, therefore $\dfrac{U}{R_c} = \dfrac{U_m}{R_m}$

The conductance: $G = \dfrac{1}{R_c} = \dfrac{U_m}{U \cdot R_m} = constant \cdot U_m$

The conductance is linearly proportional to the voltage dropping on the measuring resistance.
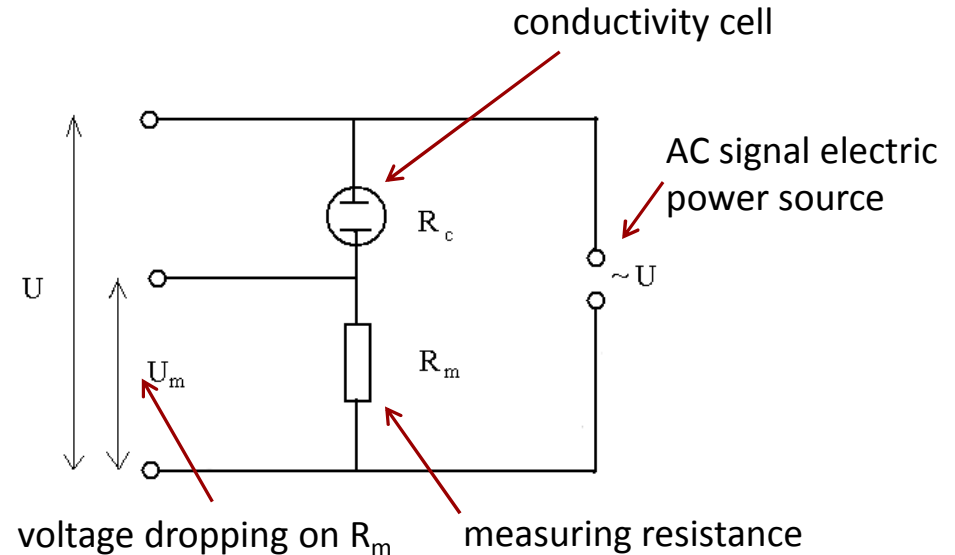
Determination of the conductivity

G can be expressed as $G = \dfrac{1}{R} = \dfrac{A}{\rho l} = \kappa \dfrac{A}{l}$

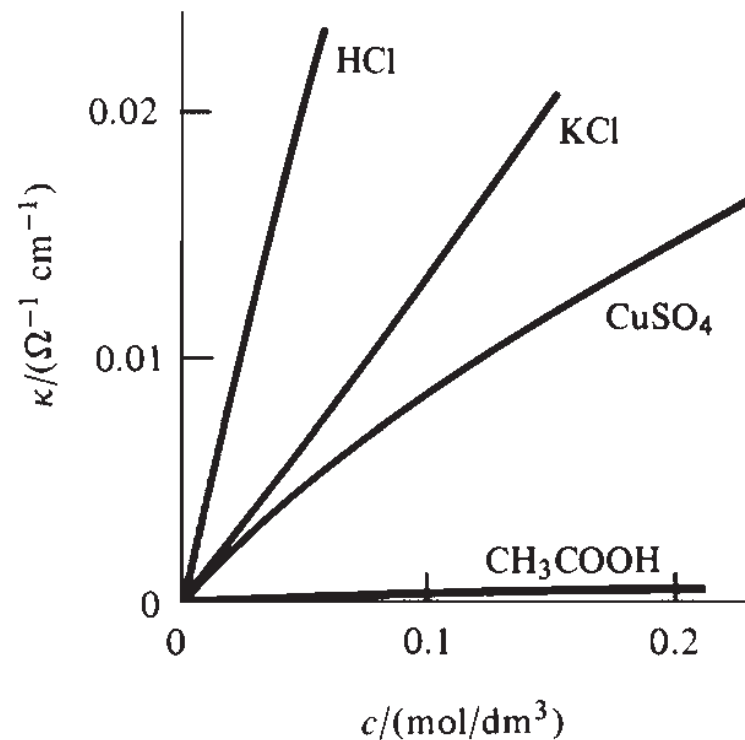Our formula in the conductance measurement can be written as:

$$\kappa \frac{A}{l} = constant \cdot U_m$$

Rearranging it to the conductivity: $\kappa = constant \cdot \dfrac{l}{A} \cdot U_m = K_{cell} \cdot U_m$

Similar to the conductance **conductivity** is also **proportinal** to the voltage drop on the measuring resistance and the proportionality factor (K_{cell}, cell constant) contains geometric parameters of the probe.

Experimental findings

The number of charge carriers per unit volume usually increases with increasing electrolyte concentration, therefore the solution's **conductivity κ increases with the electrolyte's concentration in diluted solutions**.
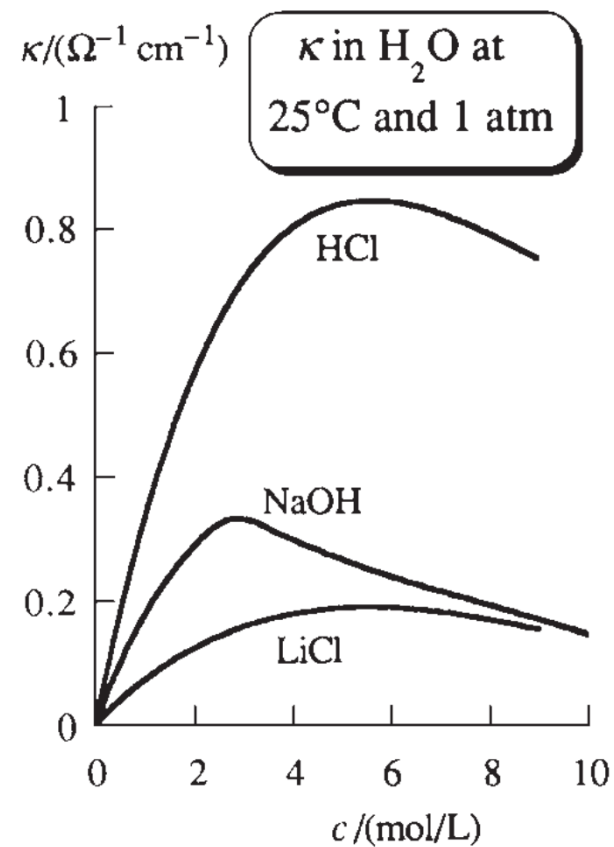
Conductivity κ versus concentration c for some aqueous electrolytes at 25°C and 1 atm.

Levine: Physical Chemistry 6th Edition
Fig. 15.21 (a)

Experimental findings

The **conductivity is not a monotonic function** of the concentration of the electrolyte even for strong electrolites in a wide range of concentration!

Conductivity versus concentration for some strong electrolytes in water at 25°C and 1 atm.

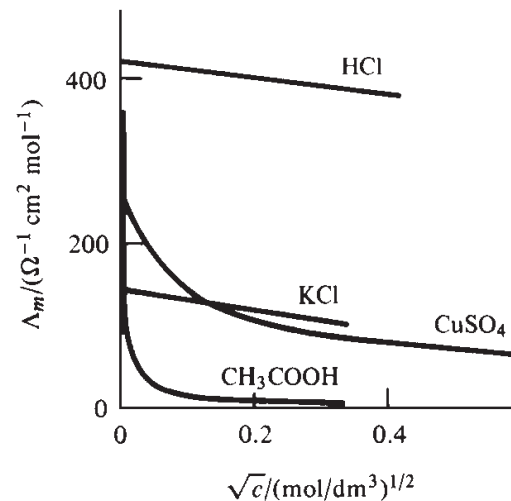Levine: Physical Chemistry 6th Edition
Fig. 15.22

Experimental findings

To get **a measure of the current-carrying ability** of a given amount of electrolyte, one defines the **molar conductivity** Λ_m of an electrolyte in solution as: $\Lambda_m = \dfrac{\kappa}{c}$ SI unit: $S \cdot m^2 \cdot mol^{-1}$

The molar conductivity is concentration and temperature dependent!
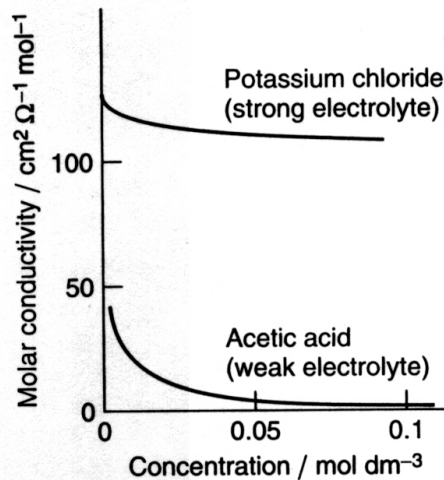
The molar conductivity decreases as c increses.

The molar conductivity is linearly proportional to the square root of c for strong electrolytes, but not linar for weaks.

Levine: Physical Chemistry 6th Edition
Fig. 15.21 (*b*)
Molar conductivity *m* versus $c^{1/2}$ for these solutions.

Contributions of individual ions
to the current density

The current density in an electrolyte solution is the sum of the current densities carried by the individual ions:

$$j = \sum_i j_i$$

When electric field is applied ions start to speed up and very soon reach a **constant terminal speed**, called **drift speed (v_i)**. (Due to the force balance of the friction force resisting the movement of ions and the electric field force accelerating them.)

The drift speed of an ion depends on the electric field strength, the ion, the solvent, T, p, and the concentrations of all the ions in the solution.

Therefore $j_i = |z_i| F c_i v_i$ and

$$j = \sum_i |z_i| F c_i v_i$$

Contributions of individual ions to the current

Since $j = \kappa \cdot E$:

$$\kappa = \sum_i |z_i| F\, c_i \frac{v_i}{E}$$

At fixed concentration κ is independent of E, therefore v_i/E is constant.
We call it **electric mobility if ion i (**or **ionic mobility)**: $u_i = \frac{v_i}{E}$

In other words: the drift speed is proportional to the electric field strength and the prorpotionality constant is the electric mobility: $v_i = u_i E$

Defining the contribution of ion i to the conductivity $\kappa_i = |z_i| F c_i u_i$:

$$\kappa = \sum_i |z_i| F c_i u_i = \sum_i \kappa_i$$

Similar to the molar conductivity we can define the molar conductivity of ion i ($\lambda_{m,i}$) as

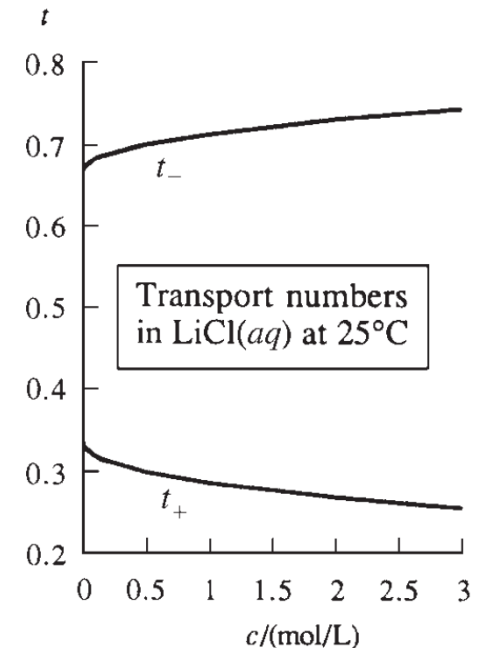$$\lambda_{m,i} = \frac{\kappa_i}{c_i}$$

The transport number

Participation of each ion to the electric current is a expressed by a fraction, called **transport number**:

$$t_i = \frac{j_i}{j} = \frac{\kappa_i}{\kappa} = \frac{|z_i|Fc_iu_i}{\sum_i |z_i|Fc_iu_i}$$

The transport number of an ion can be calculated from its mobility and the conductivity.

The sum of the transport numbers of all the ionic species in solution must be 1.

Levine: Physical Chemistry 6th Edition
Fig. 15.26
Cation and anion transport numbers versus concentration for LiCl(aq) at 25 °C and 1 atm.

Contributions of individual ions to the current

Ioninc mobilities extrapolated to infinite dilution in water at 25 °C and 1 atm.

ion					H_3O^+	Li^+	Na^+	Mg^+	OH^-	Cl^-	Br^-	NO_3^-
$10^5 u^\infty/(cm^2 V^{-1} s^{-1})$					363	40	52	55	206	79	81	74

Levine: Physical Chemistry 6th Edition
Section 15.6

Hydroxonium and hydroxide ions show abnormally high mobilities!

Special „moving" mechanisms, the prototrope mobility. The basic concept of it:
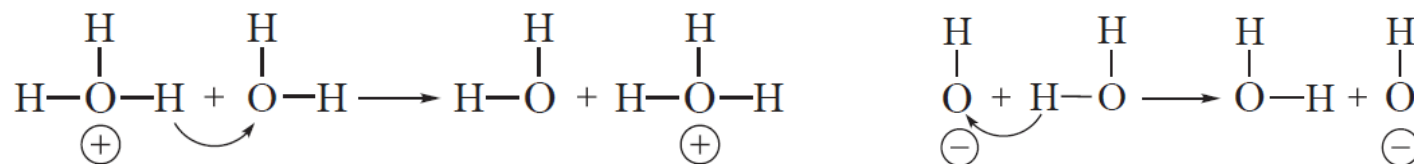
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Smaller values for cations: more hydrated than anions.

Calculation of the drift speedeffective?

Problem: Give the drift speed of potassium ion if the electric field strength in an electrolysis experiment is 8.8 V/cm if the ionic mobility of K$^+$ ion is $64.5 \cdot 10^{-5} \frac{cm^2}{Vs}$!

$$v_i = u_i E = 64.5 \cdot 10^{-5} \frac{cm^2}{Vs} \cdot 8.8 \frac{V}{cm} = 0.005676 \frac{cm}{s} \approx 0.0057 \frac{cm}{s}$$

Dependence of the drift speed and ionic mobility on the ion radius

Under stationary conditions: $F_{\text{friction}} = F_{\text{field}}$

According to the Stoke's relation (TT lecture p4) $F_{\text{friction}} = 6\pi\eta r v$, where η is the viscosity, r the ion radius, v the movement speed.
The electric field force: $F_{\text{field}} = |z|eE$, where z is the charge number of the ion.

$$v = \frac{|z|eE}{6\pi\eta r}$$

Substituting it to the equations of conductivity and ioninc mobility:

$$\kappa_i = |z_i|Fc_i\frac{v_i}{E} = \frac{|z_i|Fc_i}{E}\frac{|z_i|eE}{6\pi\eta r_i} = \frac{|z_i|^2 eFc_i}{6\pi\eta r_i}$$

$$u_i = \frac{|z_i|e}{6\pi\eta r_i}$$

Which ionic radius is effective?

Problem: Estimate the radii of Na^+ if the viscosity of water at 25 °C is 0.89·10⁻³ Ns/m² if the ionic mobility of Na^+ ion is $52 \cdot 10^{-5} \frac{cm^2}{Vs}$!

$$r_{Na^+} = \frac{|z_i|e}{6\pi\eta u_i} = \frac{1 \cdot 1.6 \cdot 10^{-19} \text{ C}}{6\pi \cdot 0.89 \cdot 10^{-3} \text{ Ns/m}^2 \cdot 52 \cdot 10^{-5} \cdot (10^{-2}\text{m})^2/V^{-1}s^{-1}} = 1{,}83 \cdot 10^{-10} \text{ m}$$

Experimental data: $r_{Na^+} = 102 \text{ pm} = 1{,}02 \cdot 10^{-10} \text{ m}$

Why is this difference? The sodium ion is surrounded by water molecules, so this radius is not a the radius of a free ion, but that of the hydrated one.

$$u_i = \frac{|z_i|e}{6\pi\eta r_i}$$ ⟵ the radius of the hydrated ion
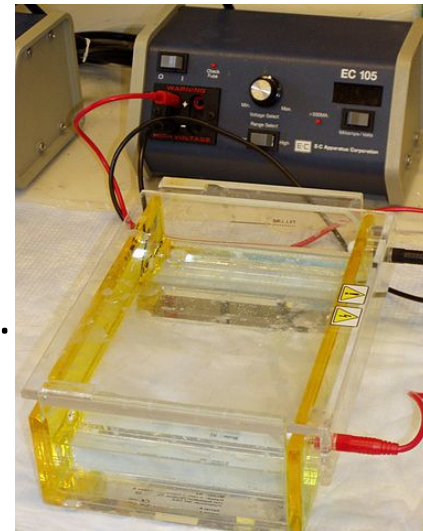
Electrophoresis

Electrophoresis: migration of charged polimer molecules (typically polyelectrolytes) and charged colloid particles in electric field.

Can separate proteins, nucleic acids.

Commonly it is not carried out in free solvent, but in gels
(**gel electrophoresis**).
In free solvent convection flows can start destroying the effect of separation.

Isoelectric focusing: Let us keep a pH gradient in the gel.
Each molecule migrates until it reaches its isoelectric point!

Gel electrophoresis apparatus – an agarose gel is placed in this buffer-filled box and an electrical field is applied via the power supply to the rear. The negative terminal is at the far end (black wire), so DNA migrates toward the positively charged anode (red wire). *Wikipedia*

Electrophoresis

Capillary electrophoresis: the polyelectrolyte molecules move through narrow (0.01-cm inside diameter) quartz capillaries filled with a gel or a polymer solution at high concentration. Interactions between the migrating polyelectrolyte molecules and the polymer molecules lead to separation according to size.

Higher voltage can be applied, leading to faster separation.

Capillary electrophoresis is particularly suitable for automated procedures.

Detection: ultraviolet absorption or by fluorescence.