

Centre of Excellence

Training course

abc-ELECTROCHEMISTRY

Part II

2. Ionic solutions

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2. Ionic solutions

Solutions of electrolytes (especially aqueous solutions) are the most important members of the **class of ionic conductor**. We will discuss the **behaviour of dissolved ions** and their **thermodynamic properties**

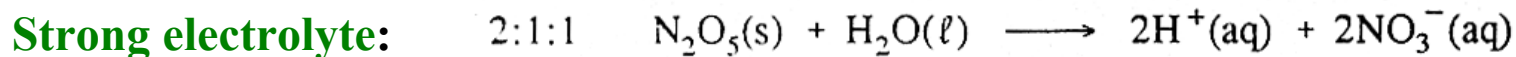
2.1 Electroneutrality

Electrolyte - substance **when dissolved** (in water or some other liquid) **or melted** produces ions and so enhances the electrical conductivity of the liquid.

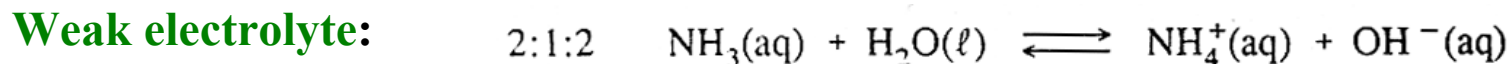
An electrolyte can be solid (NaCl), liquid (H₂SO₄) or gas (NH₃).

“Solid electrolyte” - solids that possess their own ionic conductivity.

Dinitrogen pentoxide reacts completely with water - **strong electrolyte**



Some non-ionized dissolved ammonia remains in equilibrium with its ionic products - **weak electrolyte**



Electroneutrality principle

The **forces of interaction between dissolved cations and anions** are so **large** that it is virtually **impossible to prepare solution that contains significantly unequal numbers** of positive and negative charges- **electroneutrality principle** of electrochemistry.

Example:

Solution of K_2SO_4 in water contains exactly twice as many $K^+(aq)$ ions as $SO_4^{2-}(aq)$ ions.

For solution containing only **two kinds of ions** (one - positively and one - negatively charged) holds the equality

$$2:1:3 \quad z_+c_+ = -z_-c_-$$

For solution of any composition holds the general **electroneutrality relationship**:

$$2:1:4 \quad \sum_i z_i c_i = 0$$

Apparently the **minimum number of ionic species is 2**.

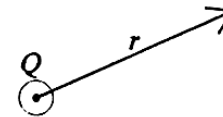
The electroneutrality principle **can be invalid for extremely small regions** - cube of edge length 200 nm contains 267 million H_2O molecule but only one ion (**H^+ or OH^-**)

Electric field

The **absence of electroneutrality** leads to **electric field gradients**. The relationship between the **field strength** and the **charge** is given by **Gauss'law** of electrostatics.

When applied to an isolated charge **Q** surrounded by a medium of permittivity ϵ , this law states that the field strength at a distance **r** from the charge is:

$$2:1:5 \quad X(r) = \frac{Q}{4\pi\epsilon r^2}$$



The **electrical potential difference** between a **point of a distance r** from the charge and a **point at infinity** is:

$$2:1:6 \quad \phi(r) - \phi(\infty) = - \int_{r, r}^{r, \infty} d\phi = \int_r^{\infty} X(r) dr = \frac{Q}{4\pi\epsilon r}$$

For example, **1 nanometre** away from a **H⁺** ion in water, this **potential difference is 18 millivolts**

The last two equations hold even if the **electric charge Q** is **not located in a single point**, provided that the charge is **spherically symmetrical** and centered at **r = 0**.

When charge is distributed in space, it is useful to think in terms of **charge density** - the **net charge** present in a small region of space **divided by the volume** of that region. **Charge density** ρ is in units C m^{-3} (coulomb per cubic meter).

From: 2:1:5 $X(r) = \frac{Q}{4\pi\epsilon r^2}$ is obtainable:

$$2:1:7 \quad 4\pi \int_0^r r^2 \rho(r) dr = Q = 4\pi\epsilon r^2 X(r)$$

because $4\pi r^2 dr$ is a **volume of a spherical shell** of radius r and thickness dr .

This equation is **perfectly general**, provided that the **charge distribution** $\rho(r)$ has **spherical symmetry** about $r = 0$.

After division by $4\pi\epsilon$ and differentiation with respect to r is obtained:

$$2:1:8 \quad \frac{r^2 \rho(r)}{\epsilon} = \frac{d}{dr} r^2 X(r) = - \frac{d}{dr} r^2 \frac{d\phi(r)}{dr}$$

Poisson's equation which applies to **spherically symmetric systems**. This important equation explains how the **potential profile** $\phi(r)$ is related to **charge density** in regions where electroneutrality does not hold.

The absence of local electroneutrality in an ionic solution arises from an imbalance in the numbers of cationic and anionic charges.

When **several ionic species** share occupancy of a region the charge density is given by:

$$2:1:9 \quad \rho = N_A \sum_i Q_i c_i = F \sum_i z_i c_i = F \sum_{\text{cations}} z_i c_i - F \sum_{\text{anions}} |z_i| c_i$$

Where:

Q_i and **c_i** denote the **charge** and the **concentration** of an ion

z_i the **charge number**.

Departures from electroneutrality in ionic solution are either small in extent or small in magnitude.

The most sensitive **chemical methods** can **not detect** any disparity between $\sum z_+ c_+$ and $\sum |z_-| c_-$

The electrical effects can be nevertheless pronounced

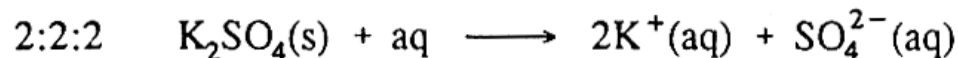
2.2 Ionic strength

In the **SI system** the **unit of concentration** is **mol m⁻³** which corresponds to **millimolar (mM)** in the more familiar chemists units, so that **1 mol m⁻³ = 1 mM**. Concentrations of interest in the electrochemistry range from about **10⁻³ mol m⁻³** to about **10³ mol m⁻³**

Another **quantity with the same unit** as concentration is an **ionic strength** of the solution - μ . It is defined as one half of the sum of all the ionic concentrations, each concentration being first multiplied by the square of its charge number

$$2:2:1 \quad \mu = \frac{1}{2} \sum_i z_i^2 c_i$$

Example: Dissolving 0.17425 g of K₂SO₄ in water to make 1 l solution (**1 mM**)



The concentration of K⁺(aq) and SO₄²⁻(aq) ions will be

$$2:2:3 \quad c_+ = 2.0000 \text{ mol m}^{-3} \quad \text{and} \quad 2:2:4 \quad c_- = 1.0000 \text{ mol m}^{-3}$$

respectively, while the **ionic strength** is

$$\begin{aligned} 2:2:5 \quad \mu &= \frac{1}{2} [1^2(2.0000 \text{ mol m}^{-3}) + (-2)^2(1.0000 \text{ mol m}^{-3})] \\ &= 3.0000 \text{ mol m}^{-3} \end{aligned}$$

The **ionic strength** of the solution is the most important parameter in **determining** such properties of the component ions as their **activities** and **mobilities**.

Consider a solution containing a variety of ions of different charges.

Imagine that there are **differences of electrical potential throughout this solution** and that one region has a **potential** ϕ_I , while a second region has a **potential** ϕ_{II} .

Cations will be attracted into the **region of more negative potential**, while **anions** will favour the **more positive region**.

The **tendency of the ions to segregate** in this way will be **opposed by the jostling** of the solvent molecules, which has a homogenising effect.

At equilibrium a **compromise** is achieved **between these competing tendencies**. **Boltzmann's distribution law**, which applies in many fields of physical sciences, addresses **equilibrium distribution** such as this.

According to the **Boltzmann's distribution law** the ratio of the concentrations c_i^{II} and c_i^{I} of species **i** in two regions is linked to $w_i^{\text{I} \rightarrow \text{II}}$ by the relationship:

$$2:2:6 \quad \frac{c_i^{\text{II}}}{c_i^{\text{I}}} = \exp \left\{ - \frac{w_i^{\text{I} \rightarrow \text{II}}}{k_B T} \right\}$$

$w_i^{\text{I} \rightarrow \text{II}}$ is the **minimum amount of non-chemical work** required to take one member of the species from region I to region II.

Here k_B is the **Boltzmann's constant** having the value $1.3807 \times 10^{-23} \text{ J K}^{-1}$, and **T** is the temperature .

The work required to carry the ion of charge Q_i from a region of potential ϕ_{I} to one of potential ϕ_{II} is simply the **product** $Q_i(\phi_{\text{II}} - \phi_{\text{I}})$ **of the charge and the potential difference**

Since $Q_i = z_i Q_e = z_i F / N_A$ we have

$$2:2:7 \quad \frac{c_i^{\text{II}}}{c_i^{\text{I}}} = \exp \left\{ - \frac{z_i F (\phi_{\text{II}} - \phi_{\text{I}})}{N_A k_B T} \right\}$$

The product $N_A k_B$ of **Avogadro's and Boltzmann's constants** is itself a constant known as **gas constant R**

$$\mathbf{R} = 8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$$

Therefore

$$2:2:8 \quad c_i^{\text{II}} = c_i^{\text{I}} \exp \left\{ - \frac{z_i F (\phi_{\text{II}} - \phi_{\text{I}})}{RT} \right\}$$

Important equation - the **equilibrium ion distribution law** - relates the **disparity of the equilibrium concentrations** of an ion between two regions to the **electrical potential difference** between those regions

(for example the low predict a 48% enrichment in the concentration of a **singly charged anion** by a 10.0 mV difference).

From 2:2:8
$$c_i^{\text{II}} = c_i^{\text{I}} \exp \left\{ - \frac{z_i F (\phi_{\text{II}} - \phi_{\text{I}})}{RT} \right\}$$

can be obtained (after multiplication by Fz_i):

2:2:9
$$Fz_i c_i^{\text{II}} \exp \left\{ \frac{z_i F (\phi_{\text{II}} - \phi_{\text{I}})}{2RT} \right\} = Fz_i c_i^{\text{I}} \exp \left\{ - \frac{z_i F (\phi_{\text{II}} - \phi_{\text{I}})}{2RT} \right\}$$

The quantity RT/F has dimension of a voltage. At 25.00°C

2:2:10
$$\frac{RT}{F} = \frac{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}{96485 \text{ C mol}^{-1}} = 25.693 \text{ mV}$$

If $z_i(\phi_{\text{II}} - \phi_{\text{I}})/2$ is small compared with the above value, as is often the case, it is legitimate to expand the exponential function in 2:2:9, using

2:2:11
$$\exp \{y\} = 1 + y + \frac{y^2}{2} + \frac{y^3}{6} + \dots$$

Ignoring all but the first two terms this leads to:

$$\begin{aligned}
 2:2:12 \quad Fz_i c_i^{\text{II}} + \left[\frac{F^2(\phi_{\text{II}} - \phi_{\text{I}})}{RT} \right] \frac{z_i^2 c_i^{\text{II}}}{2} \\
 \approx Fz_i c_i^{\text{I}} - \left[\frac{F^2(\phi_{\text{II}} - \phi_{\text{I}})}{RT} \right] \frac{z_i^2 c_i^{\text{I}}}{2}
 \end{aligned}$$

After summing over all the ions and using for charge density

$$2:1:9 \quad \rho = N_A \sum_i Q_i c_i = F \sum_i z_i c_i = F \sum_{\text{cations}} z_i c_i - F \sum_{\text{anions}} |z_i| c_i$$

and for the ionic strength

$$2:2:1 \quad \mu = \frac{1}{2} \sum_i z_i^2 c_i$$

we obtain

$$2:2:13 \quad \rho_{\text{II}} + \left[\frac{F^2(\phi_{\text{II}} - \phi_{\text{I}})}{RT} \right] \mu_{\text{II}} \approx \rho_{\text{I}} - \left[\frac{F^2(\phi_{\text{II}} - \phi_{\text{I}})}{RT} \right] \mu_{\text{I}}$$

If the **difference in the potential** between regions I and II is **as small as** has been assumed, there will be a **very little difference in the ionic strengths** between the regions and therefore μ_{I} and μ_{II} **may be replaced by a common value μ** .

After this replacement
(common μ)

$$2:2:13 \quad \rho_{II} + \left[\frac{F^2(\phi_{II} - \phi_I)}{RT} \right] \mu_{II} \approx \rho_I - \left[\frac{F^2(\phi_{II} - \phi_I)}{RT} \right] \mu_I$$

can be reshaped:

$$2:2:14 \quad \frac{\rho_{II} - \rho_I}{\phi_{II} - \phi_I} \approx - \frac{2F^2}{RT} \mu$$

It clearly shows the **role of the ionic strength** - it determines the **extend to which a potential differences induces a charge density difference**.

In very large regions of the electrolyte solution electro-neutrality is guaranteed. If **I** is such a **electroneutral region**, than $\rho = 0$. If we agree to measure potential elsewhere with respect to the average potential in region **I**, so that we may set $\phi = 0$.

The equation 2:2:14 reduces (the subscript “**II**” is redundant) to:

$$2:2:15 \quad \frac{\rho}{\phi} \approx - \frac{2F^2}{RT} \mu$$

which is one of the **cornerstones of Debye- Hueckel- theory**.

It is based on the assumption that the magnitude of $z_i \phi$ is **small** compared with 26 mV.

2.3 Activities

Activity - useful notion in electrochemistry

To every chemical distinct species can be assigned an activity - reflecting its immediate environment.

Activity of a species in a certain location reflects its “restlessness” there.

The greater the activity, the more eager is the species to leave.

Three ways to display restlessness of a species:

- to **move to adjacent location** where its activity is lower (diffusion to region of lower concentration)
- **travel to a joining phase** (precipitation from solution)
- the amount of species may **diminish by virtue of a chemical (or electrochemical) reaction**

transport into a more dilute region	}	{	ways of
transfer to an adjoining phase			lowering
chemical or electrochemical reaction			activity

In each of the above cases, the activity determines not only the **extent** to which the species disappear but also the **rate** of its disappearance.

The activity is manifested both thermodynamically and kinetically.

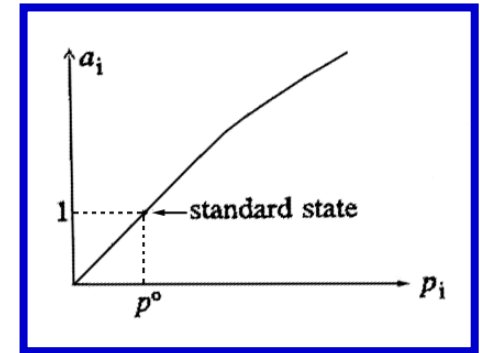
Standard state - the activity of a species measures its restlessness in some **state of interest** compared to its restlessness in a **standard state**.

Activities are **pure numbers** (no dimensions or units) - they are ratios.

Activities are **affected by temperature** and to a lesser extent **by the total pressure**. Because the influence of these variables is not a major constants in electrochemistry - at first approximation we will ignore such effects - treat only systems at constant temperature and pressure (298.15 K, 100,000 Pa).

Gases

The activity a_i of a gaseous species i depends on its partial pressure p_i and is accurately proportional to p_i except at rather high pressures.



The **standard state for a gas** is chosen to be **pure gas at pressure of 100,000 pascals** (1 bar). Because the domain of proportionality generally extends to much higher pressures than this, the relationship

$$2:3:1 \quad a_i = \frac{p_i}{p^o} \quad (i = \text{gas}) \quad \text{where } p^o = 100,000 \text{ Pa}$$

holds accurately for gases in the pressure range of general interest in electrochemistry

Liquids

The **standard state** for species in a liquid state is the **pure liquid**.

The activity of the solvent remains close to unity even for solutions of quite high concentrations ($a_{\text{H}_2\text{O}} = 1.004$ in aqueous **KCl** solution of concentration 2000 mol m^{-3}).

$$2:3:2 \quad a_i \approx 1 \quad (i = \text{solvent})$$

Solid

The **standard state** for a species in a **solid phase** is the **pure solid**.

In electrochemistry the solids are mostly **pure elements** or compounds and their activities are equal to unity.

$$2:3:3 \quad a_i = 1 \quad (i = \text{pure solid})$$

Examples:

Activity of Ag in a piece of pure silver metal is one ($a_{\text{Ag}} = 1$).

In silver-gold alloy, however, a_{Ag} is less than one.

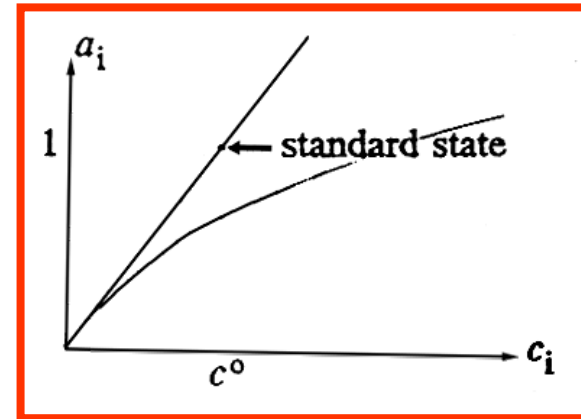
Activities of very thin layers of metals, such as newly electrodeposited films, often differ from unity

Solutes

Activity of a solute depends on its concentration, being proportional to concentration at sufficient dilution.

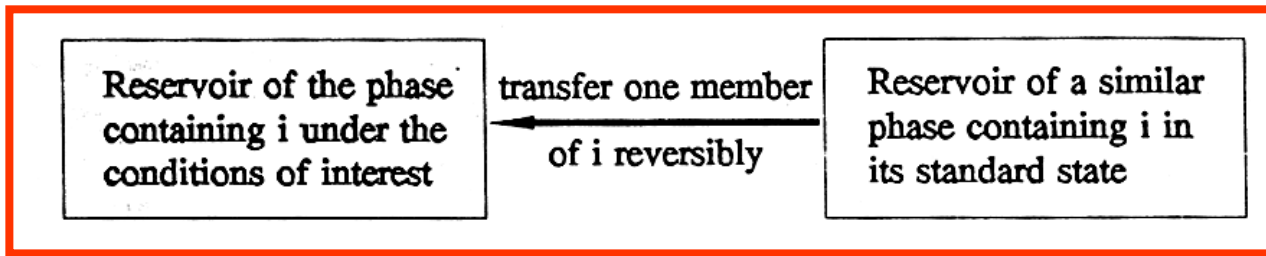
The **region of linearity** of a_i versus c_i graph is **rather limited** especially for **ionic solutes**.

The **standard state** is chosen as a **hypothetical state** - it corresponds to what the behaviour of the solute would have been at the standard concentration c^\ominus if the **linear relationship** had been maintained up to that concentration. The activity of the solute therefore is:



$$2:3:4 \quad a_i = \frac{\gamma_i c_i}{c^\ominus} \quad (i = \text{solute}) \quad \text{where } c^\ominus = 1000 \text{ mol m}^{-3}$$

where γ_i is a **correction factor**, known as the **activity coefficient** to take account of the **departure from the linearity**. The activity coefficient γ_i of a solute at any concentration c_i equals to its **actual activity** a_i divided by the “**ideal activity**” c_i/c^\ominus . The concentration of an **ideal solution** in which the **solute activity** equals c_i/c^\ominus is **often employed in the thermodynamic** arguments.



Formal definition of activity can be illustrated by the above diagram, in which one atom, molecule or ion (as the case may be) is transferred from the interior of a **standard phase** to the interior of the **phase of interest**.

If w_i is the minimum net work that must be expended to achieve this transfer than the activity of species in the **destination phase** is defined as:

$$2:3:5 \quad a_i = \exp\left\{\frac{w_i}{k_B T}\right\}$$

Alternatively, in the **equivalent language of thermodynamics** the activity a_i of the left hand reservoir is:

$$2:3:6 \quad a_i = \exp\left\{\frac{\Delta G}{RT}\right\}$$

If the transfer of **1 mole** of **i** in the direction of the arrow increases the **total Gibbs energy** (or **free energy**) of the system (both reservoirs) by ΔG .

The reservoirs in the previous diagram are imagined as **huge enough** - so large that the transfer does **not significantly** alter the **composition** of the two phases, or any other of their **intensive properties**. The last restriction causes a problem when **i** is an ion.

Whereas it may be possible to *imagine* the transfer of such a small number of ions into such a large reservoir that no significant change in the electrical potential occurs, experiments with this objective are not feasible.

One practical effect of this **difficulty** is to prevent the **measurement of individual ionic activities**.

A quantity that **can be measured** is the **mean ionic activity** a_{\pm} of a cation and an anion defined by

$$2:3:7 \quad a_{\pm} = \left(\frac{a_-^{z_+}}{a_+^{z_-}} \right)^{\frac{1}{z_+ - z_-}} = (a_-)^{\frac{z_+}{z_+ + |z_-|}} (a_+)^{\frac{|z_-|}{z_+ + |z_-|}}$$

z_+ and z_- are the charge numbers of the cation and the anion.

Example:

the **mean ionic activity** of Al^{3+} and SO_4^{2-} ions is $a_{\pm} = a_-^{3/5} a_+^{2/5}$.

The inability to measure the individual ionic activity causes less difficulty than might be supposed.

It turns out that **mean ionic activities are what one often needs.**

Activity coefficients of a single ion are also immeasurable.

We can measure only a **mean ionic activity coefficient**, given by:

$$2:3:8 \quad \gamma_{\pm} = \frac{a_{\pm} c^{\circ}}{c_i} = \left(\frac{\gamma_-^{z_+}}{\gamma_+^{z_-}} \right)^{\frac{1}{z_+ - z_-}} = (\gamma_-)^{\frac{z_+}{z_+ + |z_-|}} (\gamma_+)^{\frac{|z_-|}{z_+ + |z_-|}}$$

2:4 Solutions of extremely low ionic strength

Very small value of μ means that the **solution contain few ions** - the distance x between two ions is large. The force of repulsion between two ions is given by **Coulomb's Law**

$$2:4:1 \quad f_{12} = \frac{Q_1 Q_2}{4\pi\epsilon x^2} = \frac{z_1 z_2 Q_e^2}{4\pi\epsilon x^2}$$

Where Q_1 and Q_2 are the **charges** of the two ions and ϵ is the **permittivity** of the medium. The **inverse-square dependence on distance** means that f_{12} will be **very small** in the case of **very dilute solutions**, so that the ions behave essentially independently of each other.

The thermodynamic consequence of the independence of the ions in solutions of **extremely low ionic strength** is that the **activity of each ionic species corresponds accurately with its concentration**

$$2:4:2 \quad a_i = \frac{c_i}{c^\circ} \quad \text{where } c^\circ = 1 \text{ molar} = 10^3 \text{ mol m}^{-3}$$

When **SI units** of concentration are used, a_i and c_i differ numerically by factor of **10^3** (thermodynamic activities are based on standard concentration c° of **1 mole per litre**)

Replacements for activities

Species i	Activity replacement
pure solid	$a_i = 1$
pure liquid	$a_i = 1$
pure gas or component of a gas mixture	$a_i \approx p_i/p^\circ$ ($p^\circ = 10^5 \text{ Pa}$)
solvent	$a_i \approx 1$
nonionic solute at low or moderate concentration	$a_i \approx c_i/c^\circ$ ($c^\circ = 10^3 \text{ mol m}^{-3}$)
nonionic solute at moderate or high concentration	$a_i = \gamma_i c_i/c^\circ$ (γ_i must be measured)
ionic solute in a solution of extremely low ionic strength	$a_i \approx c_i/c^\circ$
ionic solute in aqueous solution of low or moderate concentration	$a_i \approx \frac{c_i}{c^\circ} \exp \left\{ -z_i^2 \sqrt{\frac{\mu}{727 \text{ mol m}^{-3}}} \right\}$
ionic solute in a solution of moderate or high concentration	$a_i = \gamma_i c_i/c^\circ$ (γ_i is a part of γ_{\pm} , which must be measured)
Langmuirian adsorbate	$a_i = \Gamma_i/(\Gamma_i^{\max} - \Gamma_i)$

2.5 Solutions of moderate ionic strength

Extremely dilute ionic solutions - ions distributed randomly throughout the liquid phase. At higher ionic strength - this is not the case. **Debye - Hueckel theory** - attention on the **ionic atmosphere** around a “central ion”. If the central ion is a cation, the potential in the vicinity of the ion will be more positive than the average potential of the solution. Into this region other ions will periodically come in and out because of thermal motion (**Brownian movement**).

The Boltzmann distribution law show that **ions of sign opposite** to that of the central ion **will tend to stay longer** than those of like sign. The time-averaged effect will be - **spherically symmetric zones of opposite charge** around the ion - ionic atmosphere. For the ionic activity coefficient in aqueous solutions at 25⁰ C.

$$2:5:11 \quad \gamma_i = \exp\left\{-z_i^2 \sqrt{\frac{\mu}{727 \text{ mol m}^{-3}}}\right\} \quad \text{Debye - Hueckel theory}$$

Activity coefficient of the ion **depends** on its **charge number** and on the **ionic strength** μ of the solution, but not directly on the concentration of the ion. The **activity coefficient** decreases with the increase of μ .. For the **mean ionic activity coefficient** of a **cation-anion pair in aqueous solutions** at 25⁰ C

$$2:5:12 \quad \gamma_{\pm} = \exp\left\{z_+ z_- \sqrt{\frac{\mu}{727 \text{ mol m}^{-3}}}\right\}$$

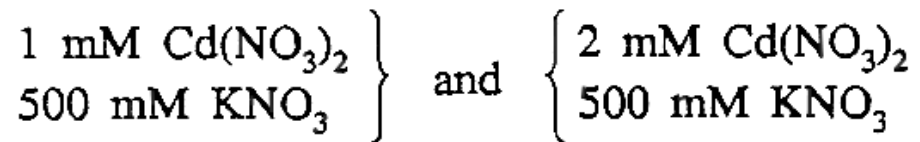
2.6 Solutions of high ionic strength

Activity coefficients are less predictable and must usually be measured than calculated.

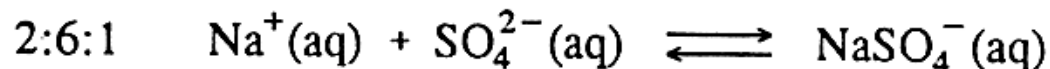
At very high μ values the **activity coefficients** often increase with ionic strength μ . This is explained with **immobilisation of the solvent in the solvating ions**.

The **properties of the ions are determined from the ionic strength** rather than the details of the solution composition - **activity coefficient** of an ion that is a **minority component** of a concentrated ionic solution is effectively independent of that particular ions concentration.

Example: the values $\gamma_{\text{Cd}^{2+}}$ are **virtually identical** in the two aqueous solutions



Ion pairing - phenomenon encountered in concentrated ionic solutions - due to the **interionic attraction between the cation and an anion in close proximity** - temporary union of the two ions into a single entity



Seawater

i	$c_i / \text{mol m}^{-3}$
Cl^-	554.1
Na^+	469.7
Mg^{2+}	47.0
SO_4^{2-}	15.3
K^+	9.9
Ca^{2+}	9.5
NaSO_4^-	6.1
HCO_3^-	1.6
Br^-	0.7
MgHCO_3^+	0.5

Example of ionic solution containing high concentration of Na^+ and SO_4^{2-} , and therefore a significant NaSO_4^- concentration is sea water.

The MgHCO_3^+ species is also an ion pair formed from HCO_3^- anion and Mg^{2+} cation.

One could even regard HCO_3^- itself as an ion pair formed from H^+ and CO_3^{2-} though it is not usually so classified

2.7 Equilibria in ionic solutions

Equilibrium may occur in ionic solutions or at their boundaries with adjacent phases. Other type of equilibrium arises as a consequence of:

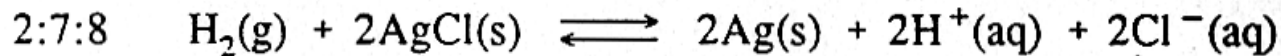
- incomplete dissociation of weak electrolytes 2:7:1 $\text{CH}_3\text{COOH}(\text{aq}) \rightleftharpoons \text{CH}_3\text{COO}^-(\text{aq}) + \text{H}^+(\text{aq})$
- limited solubility of a salt 2:7:2 $\text{AgCl}(\text{s}) \rightleftharpoons \text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq})$
- limited solubility of a base 2:7:3 $\text{HgO}(\text{s}) + \text{H}_2\text{O}(\ell) \rightleftharpoons \text{Hg}^{2+}(\text{aq}) + 2\text{OH}^-(\text{aq})$
- proton transfers between weak acids 2:7:4 $\text{HSO}_4^-(\text{aq}) + \text{CO}_3^{2-}(\text{aq}) \rightleftharpoons \text{SO}_4^{2-}(\text{aq}) + \text{HCO}_3^-(\text{aq})$
- redox reactions 2:7:5 $3\text{I}^-(\text{aq}) + \text{ClO}^-(\text{aq}) + 2\text{H}^+(\text{aq}) \rightleftharpoons \text{I}_3^-(\text{aq}) + \text{Cl}^-(\text{aq}) + \text{H}_2\text{O}(\ell)$
- disproportionations 2:7:6 $\text{Hg}_2^{2+}(\text{aq}) \rightleftharpoons \text{Hg}(\ell) + \text{Hg}^{2+}(\text{aq})$
- autoionization of the solvent 2:7:7 $\text{H}_2\text{O}(\ell) \rightleftharpoons \text{H}^+(\text{aq}) + \text{OH}^-(\text{aq})$
 $2\text{H}_2\text{O}(\ell) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{OH}^-(\text{aq})$
- reactions involving gases 2:7:8 $\text{H}_2(\text{g}) + 2\text{AgCl}(\text{s}) \rightleftharpoons 2\text{Ag}(\text{s}) + 2\text{H}^+(\text{aq}) + 2\text{Cl}^-(\text{aq})$

One and the same thermodynamic principles apply to all these equilibria.

An **equilibrium constant K** can be established for each of them

$$2:7:9 \quad \frac{\text{product of activities of right-hand species}}{\text{product of activities of left-hand species}} = K$$

Example - the constant governing equilibrium



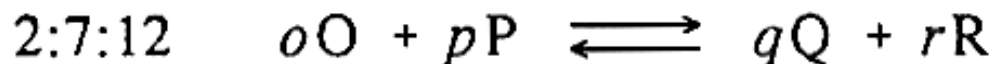
$$2:7:10 \quad \frac{a_{\text{Ag}(\text{s})}^2 a_{\text{H}^+(\text{aq})}^2 a_{\text{Cl}^-(\text{aq})}^2}{a_{\text{AgCl}(\text{s})}^2 a_{\text{H}_2(\text{g})}} = K_8 = 3.24 \times 10^7$$

Thermodynamic equilibrium constant (which is expressed in terms of activities) are **invariably dimensionless numbers** (in contrast to the case of elementary chemistry where the equilibrium constants are often expressed in terms of concentrations and may have units attached to their values).

Numerical values of equilibrium constants are calculated from “**standard Gibbs energy - ΔG^0** ” data via thermodynamic relationship

$$2:7:11 \quad K = \exp\left\{-\frac{\Delta G^0}{RT}\right\}$$

Where ΔG^0 is the **change in the standard Gibbs energy** that accompanies the **left-to-right reaction** of the equilibrium. In the general case of an equilibrium



Involving species **O, P, Q** and **R**, with **stoichiometric coefficients** **o, p, q** and **r**, the equilibrium constant is given by

$$2:7:13 \quad \left(\frac{a_Q^q a_R^r}{a_O^o a_P^p}\right)_{\text{equilibrium}} = K = \exp\left\{-\frac{\Delta G_{oO+pP \rightarrow qQ+rR}^0}{RT}\right\}$$

$$= \exp\left\{-\frac{qG_Q^0 + rG_R^0 - oG_O^0 - pG_P^0}{RT}\right\}$$

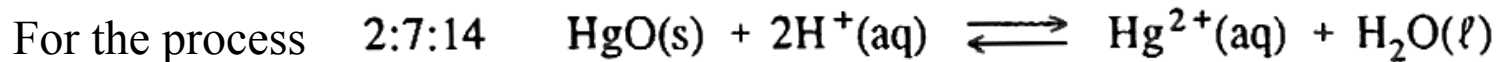
Extensive tabulations of G^0 values are available for compounds and ions in aqueous solutions.

Elements and $H^+(aq)$ ion have standard Gibbs energies of zero, by definition.

Standard Gibbs energies $G^\circ/\text{kJ mol}^{-1}$ for selected neutral and ionic species.

AgBr(s)	-95.92	Ag ⁺ (aq)	77.08	Br ⁻ (aq)	-102.76
AgCl(s)	-109.59	Al ³⁺ (aq)	-485	Cl ⁻ (aq)	-131.02
Ag ₂ O(s)	-11.20	Ca ²⁺ (aq)	-553.57	CO ₃ ²⁻ (aq)	-527.82
CaCO ₃ (s)	-1128.79	Cd ²⁺ (aq)	-77.65	Fe(CN) ₆ ³⁻ (aq)	729.4
CO ₂ (g)	-394.38	Cu ⁺ (aq)	50.3	Fe(CN) ₆ ⁴⁻ (aq)	695.08
CO ₂ (aq)	-386.2	Cu ²⁺ (aq)	65.7	HCO ₃ ⁻ (aq)	-586.98
Hg ₂ Cl ₂ (s)	-210.33	Fe ²⁺ (aq)	-78.9	HSO ₄ ⁻ (aq)	-755.91
HgO(s)	-58.54	Fe ³⁺ (aq)	-4.5	HS ⁻ (aq)	12.08
H ₂ O(l)	-237.13	Hg ₂ ²⁺ (aq)	153.57	I ⁻ (aq)	-51.65
H ₂ O ₂ (aq)	-134.03	Hg ²⁺ (aq)	164.67	I ₃ ⁻ (aq)	-51.48
H ₂ S(aq)	-27.84	In ³⁺ (aq)	-97.95	MnO ₄ ⁻ (aq)	-447.1
PbCl ₂ (s)	-313.94	Mn ²⁺ (aq)	-228.1	MnO ₄ ²⁻ (aq)	-500.6
PbO ₂ (s)	-218.96	Ni ²⁺ (aq)	-46.4	OH ⁻ (aq)	-157.24
PbSO ₄ (s)	-813.76	Pb ²⁺ (aq)	-24.18	S ²⁻ (aq)	86.34
ZnO(s)	-318.30	Tl ⁺ (aq)	-32.47	SO ₄ ²⁻ (aq)	-744.53
Zn(OH) ₂ (s)	-555.06	Zn ²⁺ (aq)	-147.19	ZnO ₂ ²⁻ (aq)	-384.4

Example:



$\Delta G^\circ = -13.92$ Kilojoules per mole (kJ/mole) - according to the data in the table

Standard Gibbs energies

Species	$G^\circ/\text{kJ mol}^{-1}$
HgO(s)	-58.54
H ⁺ (aq)	0
Hg ²⁺ (aq)	164.67
H ₂ O(ℓ)	-237.13

$$- 237.13 + 164.67 - (-58.54) - 0 = -13.92$$

Therefore the equilibrium constant is

$$\begin{aligned} (\text{RT} = 8.3145 \text{ JK}^{-1}\text{mol}^{-1} \times 298.15 \text{ K} \\ = 2.4789 \text{ kJmol}^{-1}) \end{aligned}$$

$$2:7:15 \quad \frac{a_{\text{Hg}^{2+}(\text{aq})} a_{\text{H}_2\text{O}(\ell)}}{a_{\text{HgO}(\text{s})} a_{\text{H}^+(\text{aq})}^2} = K_{14} = \exp\left\{\frac{13.92 \text{ kJ mol}^{-1}}{2.4789 \text{ kJ mol}^{-1}}\right\} = 274.6$$

Two **equilibrium constants** can be **multiplied or divided** to describe a third equilibrium

Example:

- the equilibrium constant of 2:7:3 $\text{HgO(s)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{Hg}^{2+}(\text{aq}) + 2\text{OH}^{-}(\text{aq})$

$$2:7:16 \quad \frac{a_{\text{Hg}^{2+}(\text{aq})} a_{\text{OH}^{-}(\text{aq})}^2}{a_{\text{HgO(s)}} a_{\text{H}_2\text{O(l)}}} = K_3 = 2.79 \times 10^{-26}$$

- the equilibrium constant of 2:7:7 $\text{H}_2\text{O(l)} \rightleftharpoons \text{H}^{+}(\text{aq}) + \text{OH}^{-}(\text{aq})$

$$2:7:17 \quad \frac{a_{\text{H}^{+}(\text{aq})} a_{\text{OH}^{-}(\text{aq})}}{a_{\text{H}_2\text{O(l)}}} = K_7 = 1.008 \times 10^{-14}$$

If we divide K_3 with K_7^2 we will obtain K_{14} :

$$2:7:18 \quad \frac{a_{\text{Hg}^{2+}(\text{aq})} a_{\text{H}_2\text{O(l)}}}{a_{\text{HgO(s)}} a_{\text{H}^{+}(\text{aq})}^2} = \frac{K_3}{K_7^2} = \frac{2.79 \times 10^{-26}}{(1.008 \times 10^{-14})^2} = 274.6 = K_{14}$$

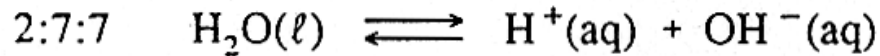
Which is in agreement with the result of 2:7:15

pH

Because of the equation:

$$2:7:17 \quad \frac{a_{\text{H}^+(\text{aq})} a_{\text{OH}^-(\text{aq})}}{a_{\text{H}_2\text{O}(\ell)}} = K_7 = 1.008 \times 10^{-14}$$

Holds for



the **activities of hydrogen and hydroxide ions** are **not independent variable** in **aqueous solutions** instead of reporting either $a_{\text{H}^+(\text{aq})}$ or $a_{\text{OH}^-(\text{aq})}$, it is more usual to cite the **pH of an aqueous solution** which is related to the **activities of the two ions by the relation**

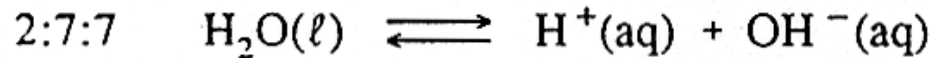
$$2:7:19 \quad \text{pH} = -\log_{10} a_{\text{H}^+(\text{aq})} = 13.997 + \log_{10} a_{\text{OH}^-(\text{aq})}$$

Before equilibrium constant relations to be related to experimental variables, it is usually necessary to replace the activity terms. The key for this is the **table “Replacement for activities”** - given before.

Replacements for activities

Species i	Activity replacement
pure solid	$a_i = 1$
pure liquid	$a_i = 1$
pure gas or component of a gas mixture	$a_i \approx p_i/p^\circ$ ($p^\circ = 10^5 \text{ Pa}$)
solvent	$a_i \approx 1$
nonionic solute at low or moderate concentration	$a_i \approx c_i/c^\circ$ ($c^\circ = 10^3 \text{ mol m}^{-3}$)
nonionic solute at moderate or high concentration	$a_i = \gamma_i c_i/c^\circ$ (γ_i must be measured)
ionic solute in a solution of extremely low ionic strength	$a_i \approx c_i/c^\circ$
ionic solute in aqueous solution of low or moderate concentration	$a_i \approx \frac{c_i}{c^\circ} \exp \left\{ -z_i^2 \sqrt{\frac{\mu}{727 \text{ mol m}^{-3}}} \right\}$
ionic solute in a solution of moderate or high concentration	$a_i = \gamma_i c_i/c^\circ$ (γ_i is a part of γ_{\pm} , which must be measured)
Langmuirian adsorbate	$a_i = \Gamma_i/(\Gamma_i^{\max} - \Gamma_i)$

If we apply its forth and fifth entries (in the table) to the self-ionization of H₂O (equilibrium 2:7:7) occurring in pure or almost pure water - equilibrium constant given by 2:7:17



$$2:7:17 \quad \frac{a_{\text{H}^+(\text{aq})} a_{\text{OH}^-(\text{aq})}}{a_{\text{H}_2\text{O}(\ell)}} = K_7 = 1.008 \times 10^{-14}$$

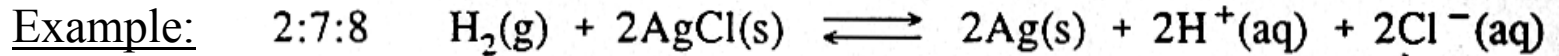
will be obtained

$$2:7:20 \quad 1.008 \times 10^{-14} = \frac{a_{\text{H}^+(\text{aq})} a_{\text{OH}^-(\text{aq})}}{a_{\text{H}_2\text{O}(\ell)}} = \frac{c_{\text{H}^+(\text{aq})} c_{\text{OH}^-(\text{aq})}}{(c^\circ)^2}$$

so that

$$\begin{aligned} 2:7:21 \quad c_{\text{H}^+(\text{aq})} c_{\text{OH}^-(\text{aq})} &= 1.008 \times 10^{-8} \text{ mol}^2 \text{ m}^{-6} \\ &= 1.008 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6} \end{aligned}$$

The latter constant is known as the **ionic product of water**



Its equilibrium constant at 25 °C is $K_g = 3.24 \times 10^7$ (equation 2:7:10).

Applying the “Table of activity replacement” we obtain:

$$2:7:22 \quad K_g = \frac{a_{\text{Ag}(\text{s})}^2 a_{\text{H}^+(\text{aq})}^2 a_{\text{Cl}^-(\text{aq})}^2}{a_{\text{AgCl}(\text{s})}^2 a_{\text{H}_2(\text{g})}} = \frac{\gamma_{\pm}^4 c_{\text{H}^+(\text{aq})}^2 c_{\text{Cl}^-(\text{aq})}^2 p^\circ}{(c^\circ)^4 p_{\text{H}_2(\text{g})}}$$

Whether or not γ_{\pm} can be replaced by the use of Debye-Hueckel theory depends on the ionic strength of the solution and the accuracy we would like to obtain.

By the use of 2:7:22 we can calculate the **equilibrium pressure of hydrogen** gas in a 30mM HCl solution in contact with silver and silver chloride.

It can be theoretically estimated γ_{\pm} as 0.85 and therefore

$$2:7:23 \quad p_{\text{H}_2(\text{g})} = \frac{(0.85)^4 (30 \text{ mol m}^{-3})^4 (10^5 \text{ Pa})}{(10^3 \text{ mol m}^{-3})^4 (3.24 \times 10^7)} = 1.3 \times 10^{-9} \text{ Pa}$$

An undetectably small pressure is obtained. This explains the experimental fact that silver does not dissolve in HCl.

2.8 Electrochemical activities

The **electrochemical activity** \tilde{a}_i of species **i** can be defined by the expression:

$$2:8:2 \quad a_i \exp \left\{ \frac{z_i F (\phi - \phi^0)}{RT} \right\} = \exp \left\{ \frac{w_i}{k_B T} \right\} = \tilde{a}_i$$

Where a_i is the “**chemical**” activity expressing the non-electric restlessness of species **i** while $\exp\{z_i F(\phi - \phi^0)/RT\}$ is a **measure of that species’ electrical restlessness**.

If two similar phases **I** and **II** contain species **i**, but at different electrochemical activities such that $\tilde{a}_i^{\text{II}} > \tilde{a}_i^{\text{I}}$, then there will be a tendency for **i** to live phase **II** in favor of phase **I**. The strength of this preference is expressed by the ratio

$$2:8:3 \quad \frac{\tilde{a}_i^{\text{II}}}{\tilde{a}_i^{\text{I}}} = \frac{a_i^{\text{II}}}{a_i^{\text{I}}} \exp \left\{ \frac{z_i F (\phi_{\text{II}} - \phi_{\text{I}})}{RT} \right\}$$

closely related to \tilde{a}_i is the quantity termed the **electrochemical potential**

The **concept of electrochemical activity** is a useful generalization of ordinary “**chemical**” activity, permitting activity laws to be extended to phases of **unequal electrical potentials**. In words, equation 2:8:2 may be written for any species, as

$$\left(\begin{array}{c} \text{chemical} \\ \text{activity} \end{array} \right) \left(\begin{array}{c} \text{electrical} \\ \text{activity} \end{array} \right) = \left(\begin{array}{c} \text{electrochemical} \\ \text{activity} \end{array} \right)$$

For **uncharged species** the electrical activity is invariably unity, so that \tilde{a}_i and a_i are identical.

For **electrons** the chemical activity equals unity, so that \tilde{a}_{e^-} contains only an electrical term.

It is only for **ions** that we need to be concerned with both contributions to \tilde{a}_i .

Contributions to activity	Chemical contribution?	Electrical contribution?
neutral species	yes	no
ions	yes	yes
electrons	no	yes

Why is it that, unlike ions in a solution, there is **no “chemical” contribution to the electrochemical activity of electrons in a metal?**

The answer is to be found in the concept from **solid-state physics**.

Electrons occupy a **“band” structure in metals**, the **bands being able to accommodate a variable number of electrons without any change in the non-electrical properties** of the metal.

Ions in a solution, in contrast, “crowd” each other and display a restlessness that increases with concentration, just as other solutes do.

2.9 Transfer equilibria

Another type of equilibrium that is important in electrochemistry involves the **transfer of an ion** between **two similar phases**.

Two phases **I** and **II**, each containing the ion **i**, but at different activities a_i^I and a_i^{II}

According to the electrochemistry the **equilibrium requires equality of the electrochemical activities** \tilde{a}_i^I and \tilde{a}_i^{II} .

According to

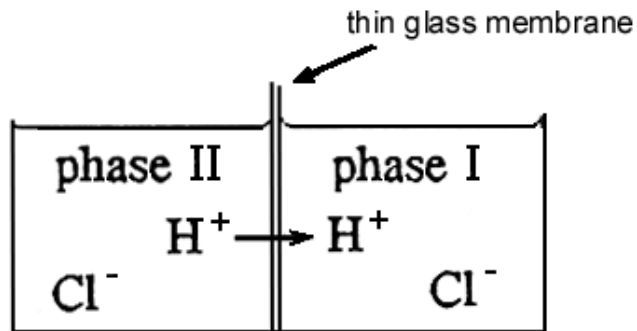
$$2:8:3 \quad \frac{\tilde{a}_i^{II}}{\tilde{a}_i^I} = \frac{a_i^{II}}{a_i^I} \exp \left\{ \frac{z_i F (\phi_{II} - \phi_I)}{RT} \right\}$$

This implies an activity ratio given by

$$2:9:1 \quad \frac{a_i^{II}}{a_i^I} = \exp \left\{ - \frac{z_i F (\phi_{II} - \phi_I)}{RT} \right\}$$

Example:

Thin membranes of certain glasses are **permeable to hydrogen ions**, but **not to other ions**.



Aqueous solutions of **HCl** are separated by thin glass diaphragm. The **concentrations** in phase I and phase II are **unequal**.

If:

$$C_{H^+}^{II} > C_{H^+}^I$$

The hydrogen ions will travel **from more concentrated side to less concentrated side** (from II to I). However the amount of transfer will be minute, because a very small departure from electroneutrality can be tolerated.

The potential of phase I becomes increasingly positive and that of II increasingly negative. The H⁺ ions transfer will end as soon as equation 2:9:1 is satisfied.

$$2:9:1 \quad \frac{a_i^{II}}{a_i^I} = \exp \left\{ - \frac{z_i F (\phi_{II} - \phi_I)}{RT} \right\}$$

This illustrates the principle of an **ion-selective membrane electrodes**.

Example:

Signal transmission by nerve impulses in animals - makes use of transfer equilibria.

Cation concentrations	Inside cell	Outside cell
$c_{K^+}/\text{mol m}^{-3}$	420	10
$c_{Na^+}/\text{mol m}^{-3}$	50	460

Though Na^+ is the dominant cation overall in animal tissue, **most cells** contain a **higher K^+** concentration.

The data in the table refer to the well studied **nerve cells of the giant axon** of the squid.

Cell walls have **limited permeability** to ions and **differences between intracellular and intercellular ionic concentration are maintained** by both active (**metabolically-fuelled “pump”**) and **passive transport** (difference in electrochemical activity).

The wall of the resting nerves have greater permeability for K^+ than to other ions and K^+ is **primarily responsible** for the **resting potential difference** that exists between the **inside and outside** of the cell.

If we assume equality of electrochemical activities for \mathbf{K}^+ ($\tilde{a}_{\mathbf{K}^+}^{\text{in}} = \tilde{a}_{\mathbf{K}^+}^{\text{out}}$) and of activity coefficient ($\gamma_{\mathbf{K}^+}^{\text{in}} = \gamma_{\mathbf{K}^+}^{\text{out}}$ - almost identical ionic strengths) than the equation 2:9:1

$$2:9:1 \quad \frac{a_i^{\text{II}}}{a_i^{\text{I}}} = \exp \left\{ - \frac{z_i F (\phi_{\text{II}} - \phi_{\text{I}})}{RT} \right\}$$

results to

$$2:9:2 \quad \phi^{\text{in}} - \phi^{\text{out}} = - \frac{RT}{F} \ln \left\{ \frac{c_{\mathbf{K}^+}^{\text{in}}}{c_{\mathbf{K}^+}^{\text{out}}} \right\} = -96 \text{ mV}$$

This result is close to the experimental value of -90 mV for the **resting potential difference of the nerve**.

The cell walls incorporate “**sodium-ion gates**” that **open in response to stimuli**. The increased permeability to \mathbf{Na}^+ ions causes the $c_{\mathbf{Na}^+}^{\text{in}}/c_{\mathbf{Na}^+}^{\text{out}}$ ratio, as well as the corresponding \mathbf{K}^+ ratio, to affect the nerve cell potential difference, which consequently rises and may transiently reach +30 mV.

The surge in potential in one portion of the nerve stimulates gate opening in the adjacent region, and so the impulses passes rapidly along a nerve.

2.10 Summary

Extremely dilute solutions of electrolytes behave not different thermodynamically than do non-ionic solutions. The activity of solute **i** being $\mathbf{c}_i/\mathbf{c}^0$ (demands imposed by the electroneutrality principle should be fulfilled).

The interionic forces present at higher concentrations affect the activity of a solute ion by a factor, the activity coefficient γ_i , that depends on the solution's ionic strength.

$$2:11:1 \quad \mu = \frac{1}{2} \sum z_i^2 c_i$$

The Debye Hueckel theory is based on the ion distribution relationship

$$2:11:2 \quad \frac{a_i^{\text{II}}}{a_i^{\text{I}}} = \exp \left\{ - \frac{z_i F (\phi_{\text{II}} - \phi_{\text{I}})}{RT} \right\}$$

and on principles of electrostatics; it leads to the low

$$2:11:3 \quad \frac{c^0 a_i}{c_i} = \gamma_i = \exp \left\{ - z_i^2 \sqrt{\frac{\mu}{727 \text{ mM}}} \right\}$$

From which ion activities in aqueous solution may be estimated.

Gibbs energy data lead to numerical values of equilibrium values of equilibrium constants

$$2:11:4 \quad K = \exp\left\{-\frac{\Delta G^\circ}{RT}\right\} = \frac{a_Q^q a_R^r}{a_O^o a_P^p} \quad \text{for } oO + pP \rightleftharpoons qQ + rR$$

for an extensive range of chemical equilibria involving ions.

After activities are replaced by more experimentally relevant quantities expressions, such as 2:11:4 provide access to use equilibrium information.

Applicable to ions and electrons, the concept of electrochemical activity is a valuable generalisation of activity for systems not at uniform electrical potential.

When applied to ions that undergo a transfer equilibrium between phases I and II of similar composition, equation 2:11:2 results.

The ratio of electrochemical activities of electrons in two conducting phases equals unity if there is transfer equilibrium. In the absence of transfer equilibrium it is given by:

$$2:11:5 \quad \frac{\tilde{a}_{e^-}^{\text{II}}}{\tilde{a}_{e^-}^{\text{I}}} = \exp\left\{-\frac{F\Delta E}{RT}\right\}$$

Here ΔE is the voltmeter-measurable voltage of phase **II** with respect to **I**, this relationship being valid irrespective of the composition of the phases.