

2106NSC

Physical & Analytical Chemistry

Thermodynamics 14

Molecular motion in liquids

Molecular motion in liquids

We have already seen in **Thermodynamics 11** that ions can be dragged through a liquid solvent by applying a **potential difference ΔE ($\Delta\phi$)** between two electrodes.

From the potential difference over a distance, we defined the **electric field $d\phi/dx$** .

The fundamental measurement in this type of experimental setup is that of the **resistance R** . The **conductance G** of a solution is the inverse of the resistance:

$$G = \frac{1}{R}$$

The conductance G increases with the cross-sectional area A and decreases with the length l ; as the constant of proportionality we introduced the **conductivity κ** :

$$G = \kappa \cdot \frac{A}{l}$$

Since the conductivity in solution will depend on the concentration of ions, we also introduced the **molar conductivity Λ_m** :

$$\Lambda_m = \frac{\kappa}{c}$$

Conductivities of electrolyte solutions

In extensive measurements with strong electrolytes (substances that are fully dissociated in solution), Kohlrausch found in the 19th century that at low concentrations, the molar conductivities vary with the square root of the concentration:

$$\Lambda_m = \Lambda_m^0 - \kappa \cdot c^{1/2} \quad \text{Kohlrausch's Law}$$

The dependence on \sqrt{c} , rather than c , is due to inter-ionic interactions. Ions of one charge may pass ions of opposite charge and thus retard their migration.

Experimentally, it could also be shown that the **limiting molar conductivity** Λ_m^0 is comprised of the independent limiting molar conductivities of the anions (λ_-) and cations (λ_+):

$$\Lambda_m^0 = \nu_+ \cdot \lambda_+ + \nu_- \cdot \lambda_- \quad \text{Law of the independent migration of ions}$$

ν is the number of ions per formula

Mobilities of ions

In an electric field $E = d\phi/dx$, where the two electrodes are at a distance $dx = l$, a particle with the charge $z \cdot e$ experiences the force:

$$F_{\text{el}} = z \cdot e \cdot E = z \cdot e \cdot d\phi / l$$

The particle is thus accelerated towards the appropriate electrode but it has to overcome friction in the liquid medium. According to Stokes, the frictional force F_{fr} of a spherical particle with radius r is related to the velocity v of the moving particle by

$$F_{\text{fr}} = f \cdot v \quad \text{with the frictional constant } f = 6 \cdot \pi \cdot \eta \cdot r \quad \text{Stokes' Law of friction}$$

η is the viscosity of the solvent

Since both forces act in opposite direction, the terminal drift speed is established, when the forces balance each other (no net force):

$$f \cdot v = z \cdot e \cdot E$$

$$v = (z \cdot e / f) \cdot E = u \cdot E \quad \text{where } u \text{ is the ion mobility}$$

Mobilities of ions

$$v = (z \cdot e / f) \cdot E = u \cdot E \quad \text{mobility } u = (z \cdot e / f) = z \cdot e / (6 \cdot \pi \cdot \eta \cdot r)$$

Units:

$$[u] = 1 \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$$

Ionic mobilities provide a link between the charge of an ion and its conductivity:

$$\lambda = z \cdot u \cdot F \quad F = N_A \cdot e \text{ is the Faraday constant}$$

We have earlier introduced the limiting molar conductivity Λ_m^0

$$\Lambda_m^0 = \nu_+ \cdot \lambda_+ + \nu_- \cdot \lambda_-$$

and can now conclude:

$$\Lambda_m^0 = \nu_+ \cdot z_+ \cdot u_+ \cdot F + \nu_- \cdot z_- \cdot u_- \cdot F$$

Mobilities and limiting molar conductivities

In the absence of any inter-ionic interactions (i.e. at low concentrations) for a symmetrical $z:z$ electrolyte, such as CuSO_4 ($\nu_+ = 1$, $\nu_- = 1$, $z_+ = z_- = z = 2$) the equation

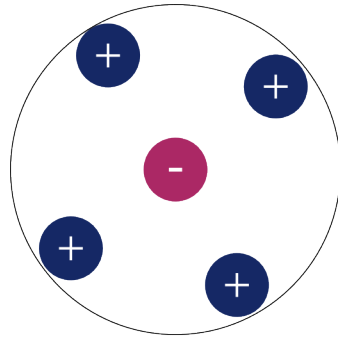
$$\Lambda_m^0 = \nu_+ \cdot z_+ \cdot u_+ \cdot F + \nu_- \cdot z_- \cdot u_- \cdot F$$

simplifies to:

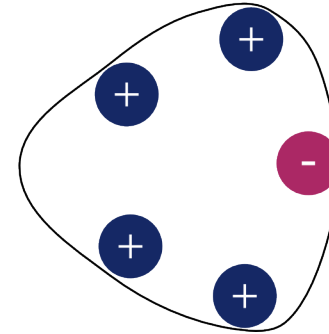
$$\Lambda_m^0 = (u_+ + u_-) \cdot z \cdot F$$

Therefore, the ionic mobilities are highly useful parameters in determining the limiting molar conductivities of electrolytes.

Ion-ion interactions



In the absence of an electric field, the ionic atmosphere surrounding a particular ion is spherical.



With an applied field, the ionic atmosphere is no longer spherical but distorted, since the centres of gravity do no longer coincide. This gives rise to a reduced mobility (**relaxation**).

The opposite direction of the movement of ionic atmosphere and the central ion also causes a viscous drag called the **electrophoretic effect**.

Ion-ion interactions

The quantitative treatment of these phenomena is complicated, but has been achieved with good experimental agreement by the Debye-Hückel-Onsager theory:

$$\kappa = A + B \cdot \Lambda_m^0 \quad \Leftrightarrow \quad \Lambda_m^0 = -A/B + 1/B \cdot \kappa \quad \text{D-H-O theory}$$

$$\Lambda_m^0 = \Lambda_m + c^{1/2} \cdot \kappa \quad \text{Kohlrausch}$$

$$A \sim \frac{z^2}{\eta \cdot \sqrt{T}}$$
$$B \sim \frac{z^3}{\sqrt{T}}$$

The Debye-Hückel-Onsager theory is in good agreement with experimental data at low molar concentrations (mM and below).

Diffusion

In the following, we will extend what we learned about the motion of ions in solvent to the motion of molecules in the absence of electric fields.

Thermodynamically, we know that if a molecule is moving from a location with the chemical potential $\mu_1 = \mu$ to another location with the chemical potential $\mu_2 = \mu + d\mu$, the work done by the system is $dW = d\mu$.

In a system, where the chemical potential depends on the position x , this results in the work

$$dW = d\mu = \left(\frac{\delta\mu}{\delta x} \right)_{p,T} \cdot dx$$

Work can generally be expressed in terms of an opposing force $dW = -F \cdot dx$, so we can define the **thermodynamic force**

$$F = - \left(\frac{\delta\mu}{\delta x} \right)_{p,T}$$

The thermodynamic force

$$F = - \left(\frac{\delta \mu}{\delta x} \right)_{p, T}$$

The thermodynamic force does not necessarily represent a real force that is pushing the particles down the slope of the chemical potential.

The thermodynamic force can represent the spontaneous tendency of molecules to disperse (2nd Law of Thermodynamics).

Fick's first law of diffusion

Consider a solution with solute of activity a ; the chemical potential is:

$$\mu = \mu^\ominus + R \cdot T \cdot \ln a \quad \text{thus} \quad \left(\frac{\delta \mu}{\delta x} \right)_{p,T} = \left(\frac{\delta \mu^\ominus}{\delta x} \right)_{p,T} + R \cdot T \cdot \left(\frac{\delta \ln a}{\delta x} \right)_{p,T}$$

If the solution is not uniform and the activity depends on the position x , then the thermodynamic force is:

$$F = - \left(\frac{\delta \mu}{\delta x} \right)_{p,T} = - \left(\frac{\delta \mu^\ominus}{\delta x} \right)_{p,T} - R \cdot T \cdot \left(\frac{\delta \ln a}{\delta x} \right)_{p,T} = - R \cdot T \cdot \left(\frac{\delta \ln a}{\delta x} \right)_{p,T}$$

If the solution is ideal, then $a = c$; and knowing that $\frac{d \ln y}{d x} = \frac{1}{y} \cdot \frac{d y}{d x}$, one obtains:

$$F = \frac{-R \cdot T}{c} \cdot \left(\frac{\delta c}{\delta x} \right)_{p,T}$$

Fick's first law of diffusion

$$F = \frac{-R \cdot T}{c} \cdot \left(\frac{\delta c}{\delta x} \right)_{p, T}$$

We can thus describe the flux of diffusing particles as motion in response to a thermodynamic force which arises from the concentration gradient.

The particles reach a steady drift speed v_{dr} , when the thermodynamic force is matched by the viscous drag.

The drift speed is proportional to the force:

$$v_{dr} \sim F$$

The particle flux J is also proportional to the drift speed:

$$J \sim v_{dr}$$

The force is proportional to the concentration gradient:

$$F \sim (dc/dx)$$

Therefore:

$$J \sim v_{dr} \sim F \sim (dc/dx)$$

=> The flux is proportional to the concentration gradient (Fick's first law of diffusion).

Fick's first law of diffusion

In terms of the concentration gradient, we can express Fick's first law using the diffusion coefficient as a constant of proportionality:

$$J = -D \cdot \frac{dc}{dx}$$

The flux is also related to the drift speed v_{dr} by:

$$J = v_{dr} \cdot c$$

Therefore:

$$v_{dr} \cdot c = -D \cdot \frac{dc}{dx} \Rightarrow v_{dr} = -\frac{D}{c} \cdot \frac{dc}{dx} = -\frac{D}{c} \cdot \left(-\frac{F \cdot c}{R \cdot T} \right) = \frac{D \cdot F}{R \cdot T}$$

The Einstein relation

$$v_{dr} = -\frac{D}{c} \cdot \frac{dc}{dx} = \frac{D \cdot F}{R \cdot T}$$

For one case, we already know the drift speed: an ion in solution has the drift speed

$$v_{dr} = u \cdot E \quad \text{with } u \text{ the mobility and } E = d\phi/dx \text{ the electric field.}$$

The force F in this case is calculated according to

$$F = N_A \cdot z \cdot e \cdot E = z \cdot F_{\text{araday}} \cdot E$$

which yields:

$$u \cdot E = \frac{z \cdot F \cdot E \cdot D}{R \cdot T} \Rightarrow u = \frac{z \cdot F \cdot D}{R \cdot T}$$

and thus:

$$D = \frac{u \cdot R \cdot T}{z \cdot F} \quad \text{Einstein relation}$$

The Einstein relation

$$D = \frac{u \cdot R \cdot T}{z \cdot F}$$

relates the diffusion coefficient D with ionic mobility u .

For a typical value of

$$u = 5 \cdot 10^{-8} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1}$$

one obtains the diffusion coefficient of

$$D = 1 \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1}$$

as a typical value of the diffusion coefficient of an ion in water.

The Stokes-Einstein equation

With $u = \frac{z \cdot F \cdot D}{R \cdot T}$ and $u = \frac{e \cdot z}{f} = \frac{z \cdot e}{6 \pi \cdot \eta \cdot r}$ (note: $v = u \cdot E = \frac{z \cdot e}{f} \cdot E$)

we obtain $\frac{z \cdot e}{6 \pi \cdot \eta \cdot r} = \frac{z \cdot F \cdot D}{R \cdot T} = \frac{z \cdot N_A \cdot e \cdot D}{R \cdot T}$

which resolves for D as:

$$D = \frac{k_B \cdot T}{6 \pi \cdot \eta \cdot r} \quad \text{Stokes-Einstein equation}$$

and relates the diffusion coefficient D of a solute of radius r with the viscosity of the medium, η .

This important equation is the basis of determination of the diffusion coefficient D with viscosity measurements. Note that there is no reference to the charge state, so all molecules can be assessed this way.

The Stokes-Einstein equation

$$D = \frac{k_B \cdot T}{6\pi \cdot \eta \cdot r}$$

Here, thermodynamic quantities (temperature, the average energy of particles $k_B \cdot T$) that relate to large numbers of particles are applied to single molecules!

It is thus not a “clean” approach, but it delivers values that agree surprisingly well with experimental data.

This important equation is the basis of determination of the diffusion coefficient D with viscosity measurements.

Note that there is no reference to the charge state, so all molecules can be assessed this way.

Suggested Reading

Hofmann, A (2016) *Introduction to Physical Chemistry*, 2nd Edition, Structural Chemistry Program, Griffith University. V.2

Atkins, PW & de Paula, J (2010) *Physical Chemistry*, 9th Edition, Oxford University Press. Sections 20.5 – 20.11 (pp. 758-774)