Lecture #6 of 17
Q: What’s in this set of lectures?
A: B&F Chapters 1, 15 & 4 main concepts:

- Section 1.1: Redox reactions
- Chapter 15: Electrochemical instrumentation
- Section 1.2: Charging interfaces
- Section 1.3: Overview of electrochemical experiments
- Section 1.4: Mass transfer and Semi-empirical treatment of electrochemical observations
- Chapter 4: Mass transfer
Looking forward… Section 1.4 and Chapter 4

- Mass transfer
- Diffusion
- Migration / Drift
- Convection
- Semi-empirical models
- Conductivity
- Transport (Transference) number
- Balance sheets
We can all label the faradaic and non-faradaic processes... but what is this new feature?

What if we just “ran out” of Cl⁻ at the electrode to oxidize?

... RECALL FROM LAST TIME...
… mass transfer in electrochemistry is concerned with the movement of material = mass (even species as small as electrons) from one location (in solution) to another, and arises from spatial differences in electric potential, chemical potential, or from volume movement (of solution)…

… We need to understand mass transfer! …
mass transfer in electrochemistry is concerned with the movement of material = mass (even species as small as electrons) from one location (in solution) to another, and arises from spatial differences in electric potential, chemical potential, or from volume movement (of solution)…

... We need to understand mass transfer! ...

... but first, because it relates directly to mass transfer, I need to introduce the governing equation for the continuity of mass, which is even more stringent than the law of the conservation of mass!
... since the continuity of mass equation is “better than” the conservation of mass law, and it is highly relevant to electrochemistry and in fact all science and engineering fields, we better know it...

... it is introduced to most undergraduate students studying chemical engineering, materials science, and physics, but only partially to chemists (first half) and mechanical engineers (second half)...

... anyway, here it is for species A along dimension $x$... Enjoy!

$$\frac{\partial c_A}{\partial t} = \sum_i R_{A,i} - \frac{\partial N_A}{\partial x}$$

... since the continuity of mass equation is “better than” the conservation of mass law, and it is highly relevant to electrochemistry and in fact all science and engineering fields, we better know it...

... it is introduced to most undergraduate students studying chemical engineering, materials science, and physics, but only partially to chemists (first half) and mechanical engineers (second half)...

... anyway, here it is for species A along dimension $x$... Enjoy!

$$\frac{\partial c_A}{\partial t}$$

rate of change of the (c)oncentration of species A with respect to (t)ime

https://en.wikipedia.org/wiki/Continuity_equation
... since the continuity of mass equation is “better than” the conservation of mass law, and it is highly relevant to electrochemistry and in fact all science and engineering fields, we better know it...

... it is introduced to most undergraduate students studying chemical engineering, materials science, and physics, but only partially to chemists (first half) and mechanical engineers (second half)...

... anyway, here it is for species A along dimension $x$... Enjoy!

$$\frac{\partial c_A}{\partial t} = \sum_i R_{A,i}$$

rate of change of the concentration of species A with respect to (t)ime

mass action (R)ate laws that effect species A, e.g. $k_2[A][B]$

... this is what chemists were taught

... it’s easy!

... and recall that these (R)ections are driven by differences in chemical potential, $\mu$, of various species, including A

https://en.wikipedia.org/wiki/Continuity_equation
... since the continuity of mass equation is “better than” the conservation of mass law, and it is highly relevant to electrochemistry and in fact all science and engineering fields, we better know it...

... it is introduced to most undergraduate students studying chemical engineering, materials science, and physics, but only partially to chemists (first half) and mechanical engineers (second half)...

... anyway, here it is for species A along dimension \( x \)... Enjoy!

\[
\frac{\partial c_A}{\partial t} = \sum_i R_{A,i} - \frac{\partial N_A}{\partial x}
\]

rate of change of the concentration of species A with respect to time

mass action (\( R \))ate laws that effect species A, e.g. \( k_2[A][B] \)

rate of change of the flux (\( N \)) of species A with respect to position (\( x \))

https://en.wikipedia.org/wiki/Continuity_equation

... what is mass flux? ... it’s easy!
Mass transfer… and also heat transfer… and momentum transfer
(1) **Migration / Drift** *(not heat as heat is not charged!)*

Flux (mol cm\(^{-2}\) s\(^{-1}\)) of **charged** species due to an electric field (electric potential)… in general, stirring does not affect this as cations and anions move in opposite directions.

(1) **Migration / Drift** *(not heat as heat is not charged!)*
Flux (mol cm\(^{-2}\) s\(^{-1}\)) of **charged** species due to an electric field (electric potential)... in general, stirring does not affect this as cations and anions move in opposite directions.

(2) **Diffusion** *(heat transport is down a temperature gradient)*
Flux of **species** due to a concentration gradient and random thermal motion (no real "force")

[Diffusion animation](http://en.wikipedia.org/wiki/Diffusion)
(1) **Migration / Drift** *(not heat as heat is not charged!)*
Flux (mol cm\(^{-2}\) s\(^{-1}\)) of **charged** species due to an electric field (electric potential)… in general, stirring does not affect this as cations and anions move in opposite directions

(2) **Diffusion** *(heat transport is down a temperature gradient)*
Flux of **species** due to a concentration gradient and random thermal motion (no real “force”)

(3) **Convection** *(heat transport is fluid/gas motion)*
Hydrodynamic movement (e.g. forced convection (stirring)) still keeps charged species near each other (Coulombic attraction)

… FYI: electro-convection occurs after ~30 sec of an electrochemical experiment
(1) **Migration**
Flux (not heat as heat is not charged!) due to an electric field (electric potential)… in general, stirring does not affect this as cations and anions move in opposite directions

(2) **Diffusion**
Flux of species due to a concentration gradient and random thermal motion (no real “force”)

(3) **Convection** *(heat transport is fluid/gas motion)*
Hydrodynamic movement (e.g. forced convection (stirring)) still keeps charged species near each other (Coulombic attraction)

… FYI: electro-convection occurs after ~30 sec of an electrochemical experiment

Mass transfer is (mostly) driven by gradients in electrochemical potential…

Mass transfer, for a charged species, sounds like a current!

How is current density ($\mathbf{J}$, A cm$^{-2}$) is related to flux ($\mathbf{N}$, mol cm$^{-2}$ s$^{-1}$)?

… well, current density has units of A cm$^{-2} = $ C cm$^{-2}$ s$^{-1}$...

… and flux has units of mol cm$^{-2}$ s$^{-1}$...

… So what do we need to equate these? …
Mass transfer, for a charged species, sounds like a current!

How is current density \( (\mathbf{J}, \text{A cm}^{-2}) \) is related to flux \( (\mathbf{N}, \text{mol cm}^{-2} \text{s}^{-1}) \)?

… well, current density has units of \( \text{A cm}^{-2} = \text{C cm}^{-2} \text{s}^{-1} \)…

… and flux has units of \( \text{mol cm}^{-2} \text{s}^{-1} \)…

… So what do we need to equate these? …

… *something with units of \( \text{C mol}^{-1} \)…*
Mass transfer is (mostly) driven by gradients in electrochemical potential…

Mass transfer, for a charged species, sounds like a current!

How is current density \( (J, \text{ A cm}^{-2}) \) is related to flux \( (N, \text{ mol cm}^{-2} \text{ s}^{-1}) \)?

… well, current density has units of \( \text{A cm}^{-2} = \text{C cm}^{-2} \text{ s}^{-1} \)…

… and flux has units of \( \text{mol cm}^{-2} \text{ s}^{-1} \)…

… So what do we need to equate these? …

… *something with units of \( \text{C mol}^{-1} \)…

\[
J_x = zF N_x \quad \text{… the Faraday constant}
\]
Mass transfer is (mostly) driven by gradients in electrochemical potential...

Mass transfer, for a charged species, sounds like a current!

How is current density ($J$, A cm$^{-2}$) is related to flux ($N$, mol cm$^{-2}$ s$^{-1}$)?

... well, current density has units of A cm$^{-2}$ = C cm$^{-2}$ s$^{-1}$...

... and flux has units of mol cm$^{-2}$ s$^{-1}$...

... So what do we need to equate these? ...

... *something with units of C mol$^{-1}$*...

$$J_x = zF N_x \quad \text{... the Faraday constant}$$

The total current density, in one-dimension, due to all charged species is,

$$J_x = zF N_x = F \sum_i z_i \left(- \frac{D_{i,x} c_i}{RT} \cdot \frac{d\bar{\mu}_i}{dx} + c_i \nu_{i,x} \right), \text{ and in 3D,}$$

$$J = zF N = F \sum_i z_i \left(- \frac{D_i c_i}{RT} \cdot \nabla \bar{\mu}_i + c_i \nu_i \right), \text{ where } \nabla \text{ is “del” (nabla)}$$

... where $D_i$ is the diffusion coefficient of species $i$ (in units of cm$^2$ s$^{-1}$), $c$ is the concentration (in units of mol cm$^{-3}$), $\bar{\mu}$ is the electrochemical potential (in units of J mol$^{-1}$), and $\nu$ is the velocity (in units of cm s$^{-1}$)
Mass transfer is (mostly) driven by gradients in electrochemical potential…

Mass transfer, for a charged species, sounds like a current!

How is current density \( (J, \text{ A cm}^{-2}) \) related to flux \( (N, \text{ mol cm}^{-2} \text{ s}^{-1}) \)?

… well, current density has units of \( \text{A cm}^{-2} = \text{C cm}^{-2} \text{ s}^{-1} \) …

… and flux has units of \( \text{mol cm}^{-2} \text{ s}^{-1} \) …

… So what do we need to equate these? …

… *something with units of C mol\(^{-1}\)* …

\[
J_x = z F N_x \quad \text{... the Faraday constant}
\]

The total current density, in one-dimension, due to all charged species is,

\[
J_x = z F N_x = F \sum_i z_i \left( -\frac{D_{i,x} c_i}{RT} \cdot \frac{d \bar{\mu}_i}{dx} + c_i v_{i,x} \right), \quad \text{and in 3D,}
\]

\[
J = z F N = F \sum_i z_i \left( -\frac{D_i c_i}{RT} \cdot \nabla \bar{\mu}_i + c_i v_i \right), \quad \text{where } \nabla \text{ is “del” (nabla)}
\]

… where \( D_i \) is the diffusion coefficient of species \( i \) (in units of \( \text{cm}^2 \text{ s}^{-1} \)), \( c \) is the concentration (in units of \( \text{mol cm}^{-3} \)), \( \bar{\mu} \) is the electrochemical potential (in units of \( \text{J mol}^{-1} \)), and \( v \) is the velocity (in units of \( \text{cm s}^{-1} \))

For derivation, see Bockris & Reddy, Modern EChem, Vol. 1, 2002, Section 4.4.15
Mass transfer is (mostly) driven by gradients in electrochemical potential...

Mass transfer, for a charged species, sounds like a current!

How is current density \( (J, \text{A cm}^{-2}) \) related to flux \( (N, \text{mol cm}^{-2} \text{s}^{-1}) \)?

... well, current density has units of \( \text{A cm}^{-2} = \text{C cm}^{-2} \text{s}^{-1} \)...

... and flux has units of \( \text{mol cm}^{-2} \text{s}^{-1} \)...

... So what do we need to equate these? ...

... something with units of \( \text{C mol}^{-1} \)...

As we will soon see, this equals mobility, \( J_x = zF N_x \) ... the Faraday constant and thus in the absence of convection...

The total current density, in one-dimension, due to all charged species is,

\[
J_x = zFN_x = F \sum_i z_i \left( -\frac{D_{i,x}c_i}{RT} \cdot \frac{d\bar{\mu}_i}{dx} + c_i v_{i,x} \right),
\]

and in 3D,

\[
J = zFN = F \sum_i z_i \left( -\frac{D_{i,c_i}}{RT} \cdot \nabla \bar{\mu}_i + c_i v_i \right),
\]

where \( \nabla \) is “del” (nabla)

... where \( D_i \) is the diffusion coefficient of species \( i \) (in units of \( \text{cm}^2 \text{s}^{-1} \)), \( c \) is the concentration (in units of \( \text{mol cm}^{-3} \)), \( \bar{\mu} \) is the electrochemical potential (in units of \( \text{J mol}^{-1} \)), and \( v \) is the velocity (in units of \( \text{cm s}^{-1} \))
mass transport/transfer of molecules to the WE in an electrochemical cell has three contributions: diffusion, migration, and convection.

the *Nernst–Planck Equation*:

\[
J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} - \frac{z_i F}{RT} D_i C_i \frac{\partial \phi(x)}{\partial x} + C_i v(x)
\]

the total *flux* of reactant *i* to a flat electrode (this is \(N_i(x)\) in many textbooks, especially engineering ones; it has units of mol cm\(^{-2}\) s\(^{-1}\))
mass transport/transfer of molecules to the WE in an electrochemical cell has three contributions: diffusion, migration, and convection.

The Nernst–Planck Equation:

\[ J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} - \frac{z_i F}{RT} D_i C_i \frac{\partial \phi(x)}{\partial x} + C_i v(x) \]

the diffusive flux of reactant \( i \) to a flat electrode where \( D_i \) is the diffusion coefficient for species, \( i \)

\( (D \) has units of \( \text{cm}^2 \text{s}^{-1} \))
mass transport/transfer of molecules to the WE in an electrochemical cell has three contributions: diffusion, migration, and convection.

The Nernst–Planck Equation:

\[ J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} - \frac{z_i F}{RT} D_i C_i \frac{\partial \phi(x)}{\partial x} + C_i v(x) \]

B&F, 1.4.2 & 4.1.8

the flux due to migration/drift of reactant \( i \) where \( z_i \) is the charge on species \( i \), and \( \partial \phi/\partial x \) is the gradient in electric potential
mass transport/transfer of molecules to the WE in an electrochemical cell has three contributions: diffusion, migration, and convection

the Nernst–Planck Equation:

$$J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} - \frac{z_i F}{RT} D_i C_i \frac{\partial \phi(x)}{\partial x} + C_i \nu(x)$$

the flux due to convection of reactant $i$ where $\nu(x)$ is the velocity profile of the solution
mass transport/transfer of molecules to the WE in an electrochemical cell has three contributions: diffusion, migration, and convection.

The Nernst–Planck Equation:

\[ J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} - \frac{z_i F}{RT} D_i C_i \frac{\partial \phi(x)}{\partial x} + C_i v(x) \]

... so, because we are adding up three contributions to the flux, which is proportional to the current (density), if we drew a circuit to represent these terms, would these be in series or in parallel?
mass transport/transfer of molecules to the WE in an electrochemical cell has three contributions: diffusion, migration, and convection

the *Nernst–Planck Equation*:

$$J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} - \frac{z_i F}{RT} D_i C_i \frac{\partial \phi(x)}{\partial x} + C_i \nu(x)$$

... so, because we are adding up three contributions to the flux, which is proportional to the current (density), if we drew a circuit to represent these terms, would these be in series or in parallel?

... in parallel... $$J_i(x) = J_1 + J_2 + J_3$$
mass transport/transfer of molecules to the WE in an electrochemical cell has three contributions: diffusion, migration, and convection.

the Nernst–Planck Equation:

$$J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} - \frac{z_i F}{RT} D_i C_i \frac{\partial \phi(x)}{\partial x} + C_i v(x)$$

B&F, 1.4.2 & 4.1.8

... so, if $J_{\text{drift}}$ is huge and $J_{\text{diffusion}}$ is small, what process dominates $J$?

... and now what if there was rapid stirring?
mass transport/transfer of molecules to the WE in an electrochemical cell has three contributions: diffusion, migration, and convection

the Nernst–Planck Equation:

\[ J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} - \frac{z_i F}{RT} D_i C_i \frac{\partial \phi(x)}{\partial x} + C_i v(x) \]

B&F, 1.4.2 & 4.1.8

... so, if \( J_{\text{drift}} \) is huge and \( J_{\text{diffusion}} \) is small, what process dominates \( J \)?

\( J_{\text{drift}} \)

... and now what if there was rapid stirring?

\( J_{\text{convection}} \)
mass transport/transfer of molecules to the WE in an electrochemical cell has three contributions: diffusion, migration, and convection.

the *Nernst–Planck Equation*:

\[ J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} - \frac{z_i F}{RT} D_i C_i \frac{\partial \phi(x)}{\partial x} + C_i v(x) \]

... again... but where did this equation for flux come from?

... who’s comfortable with me just giving you this equation?
Electrochemical potential of species $i$ in phase $\beta$ is an energy (J/mol),

$$\mu^\beta_i = \left(\frac{\partial G}{\partial n^\beta_i}\right)_{T,p,n_{j\neq i}} = \mu^\beta_i + z_i F \phi^\beta,$$

where

- $G$ (Gibbs free energy (J))
- $n_i$ (amount of species $i$ (mol))
- $\mu_i = \mu_i^0 + RT \ln a_i$ (chemical potential (J/mol))
- $z_i$ (valency of species $i$)
- $F \approx 10^5$ (Faraday constant (C/mol))
- $\phi^\beta$ (Galvani/inner electric potential (V))
- $a_i$ (activity of species $i$)

For an uncharged species $\mu_i^\beta = \mu_i^\beta$.
From before, for one species the total flux in one-dimension is

\[ N = -\frac{Dc}{RT} \cdot \frac{d\bar{\mu}}{dx} + cv, \]

where again \( D \) is diffusion coefficient (cm² s⁻¹), \( c \) is concentration (mol cm⁻³), \( \bar{\mu} \) is the electrochemical potential (J mol⁻¹), \( \nu \) is velocity (cm s⁻¹)

\[ J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} - \frac{z_iF}{RT} D_i C_i \frac{\partial \phi(x)}{\partial x} + C_i \nu(x) \]
From before, for one species the total flux in one-dimension is

$$N = -\frac{Dc}{RT} \cdot \frac{d\bar{\mu}}{dx} + cv$$, where again $D$ is diffusion coefficient (cm² s⁻¹), $c$ is concentration (mol cm⁻³), $\bar{\mu}$ is the electrochemical potential (J mol⁻¹), $\nu$ is velocity (cm s⁻¹).

Recall that $\bar{\mu}_i^{\beta} = \mu_i^{\beta} + z_i F \phi^{\beta}$ and so,

$$N = -\frac{Dc}{RT} \cdot \frac{d(\mu+z_iF\phi)}{dx} + cv$$

$$J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} - \frac{z_i F}{RT} D_i C_i \frac{\partial \phi(x)}{\partial x} + C_i \nu(x)$$
From before, for one species the total flux in one-dimension is

\[ N = -\frac{Dc}{RT} \cdot \frac{d\bar{\mu}}{dx} + c\nu, \]

where again \( D \) is diffusion coefficient (cm\(^2\) s\(^{-1}\)), \( c \) is concentration (mol cm\(^{-3}\)), \( \bar{\mu} \) is the electrochemical potential (J mol\(^{-1}\)), \( \nu \) is velocity (cm s\(^{-1}\)).

Recall that \( \bar{\mu}_i^\beta = \mu_i^\beta + z_i F \phi^\beta \) and so,

\[ N = -\frac{Dc}{RT} \cdot \frac{d(\mu+ZF\phi)}{dx} + c\nu, \]

and recall that \( \mu_i = \mu_i^0 + RT \ln a_i \) and so,

\[ N = -\frac{Dc}{RT} \cdot \frac{d(\mu^0+RT \ln a+ZF\phi)}{dx} + c\nu \]

\[ J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} - \frac{z_i F}{RT} D_i C_i \frac{\partial \phi(x)}{\partial x} + C_i \nu(x) \]
From before, for one species the total flux in one-dimension is

\[ N = -\frac{Dc}{RT} \cdot \frac{d\mu}{dx} + cv, \]

where again \( D \) is diffusion coefficient (cm\(^2\) s\(^{-1}\)), \( c \) is concentration (mol cm\(^{-3}\)), \( \mu \) is the electrochemical potential (J mol\(^{-1}\)), \( v \) is velocity (cm s\(^{-1}\))

Recall that \( \tilde{\mu}_{i}^{\beta} = \mu_{i}^{\beta} + z_{i}F\phi^{\beta} \) and so,

\[ N = -\frac{Dc}{RT} \cdot \frac{d(\mu+zF\phi)}{dx} + cv, \]

and recall that \( \mu_{i} = \mu_{i}^{0} + RT \ln a_{i} \) and so,

\[ N = -\frac{Dc}{RT} \cdot \frac{d(\mu^{0}+RT \ln a+zF\phi)}{dx} + cv, \]

and assuming \( a \approx c \),

\[ N = -Dc \cdot \frac{d(\ln c)}{dx} - \frac{zFD}{RT} c \cdot \frac{d\phi}{dx} + cv \]

\[ J_{i}(x) = -D_{i} \frac{\partial C_{i}(x)}{\partial x} - \frac{z_{i}F}{RT} D_{i}C_{i} \frac{\partial \phi(x)}{\partial x} + C_{i}v(x) \]
From before, for one species the total flux in one-dimension is

\[ N = -\frac{D c}{RT} \cdot \frac{d\bar{\mu}}{dx} + c \nu, \]

where again \( D \) is diffusion coefficient (cm\(^2\) s\(^{-1}\)), \( c \) is concentration (mol cm\(^{-3}\)), \( \bar{\mu} \) is the electrochemical potential (J mol\(^{-1}\)), \( \nu \) is velocity (cm s\(^{-1}\)).

Recall that \( \bar{\mu}^{\beta}_i = \mu^{\beta}_i + z_i F \phi^{\beta} \) and so,

\[ N = -\frac{D c}{RT} \cdot \frac{d(\mu + zF \phi)}{dx} + c \nu, \]

and recall that \( \mu_i = \mu_i^{0} + RT \ln a_i \) and so,

\[ N = -\frac{D c}{RT} \cdot \frac{d(\mu^{0} + RT \ln a + zF \phi)}{dx} + c \nu, \]

and assuming \( a \approx c \),

\[ N = -D c \cdot \frac{d(\ln c)}{dx} - \frac{zF D}{RT} c \cdot \frac{d\phi}{dx} + c \nu, \]

and finally...

\[ J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} - \frac{z_i F}{RT} D_i C_i \frac{\partial \phi(x)}{\partial x} + C_i \nu(x) \]
Diffusion coefficient \((D, \text{cm}^2\text{s}^{-1})\) – “proportionality constant relating the flux of [the] amount of [an entity to its] concentration gradient…” (IUPAC Gold Book)
Diffusion coefficient ($D$, cm$^2$ s$^{-1}$) – “proportionality constant relating the flux of [the] amount of [an entity to its] concentration gradient…” (IUPAC Gold Book)

**Fick’s first law of steady-state Diffusion:** \( N_z = -D_z \frac{dc}{dz} \), in 1D

(The second law is for non-steady-state conditions, where time is another independent variable.)
Some very important background “first”… okay, second!

**Diffusion coefficient** \((D, \text{ cm}^2 \text{ s}^{-1})\) – “proportionality constant relating the flux of [the] amount of [an entity to its] concentration gradient…” (IUPAC Gold Book)

**Fick’s first law of steady-state Diffusion:** \(N_z = -D_z \frac{dc}{dz}\), in 1D

\(D\) also exhibits Arrhenius behavior: \(D = D_0 e^{-\frac{E_a}{RT}}\)

where \(D_0\) is the maximum \(D\) (at infinite \(T\))

\(\Delta G < 0\)
Diffusion coefficient \((D, \text{cm}^2 \text{s}^{-1})\) – “proportionality constant relating the flux of [the] amount of [an entity to its] concentration gradient…” (IUPAC Gold Book)

Fick’s first law of **steady-state** Diffusion: \(N_z = -D_z \frac{dc}{dz}\), in 1D

\(D\) also exhibits Arrhenius behavior: \(D = D_0 e^{-\frac{E_a}{RT}}\)

where \(D_0\) is the maximum \(D\) (at infinite \(T\))

Some very important background “first”… okay, second!

**Adolf Eugen Fick** (1829–1901)

from Wiki
Steady-state? ...

… Initial states equilibrate using ICE, ICE Baby!

\[ A \iff B + C \]

<table>
<thead>
<tr>
<th>Reaction</th>
<th>HA</th>
<th>A(^{-})</th>
<th>H(_3)O(^{+})</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0.150 M</td>
<td>0.000 M</td>
<td>0.000 M</td>
</tr>
<tr>
<td>C</td>
<td>-x M</td>
<td>+x M</td>
<td>+x M</td>
</tr>
<tr>
<td>E</td>
<td>0.150 - x M</td>
<td>x M</td>
<td>x M</td>
</tr>
</tbody>
</table>

http://chemwiki.ucdavis.edu/Physical_Chemistry/Equilibria/Le_Chatelier%27s_Principle/Ice_Tables

http://buzzworthy.mtv.com/2012/11/14/justin-bieber-vanilla-ice-photo/
Steady-state? …

… Initial states equilibrate using ICE, ICE Baby!

\[
A \rightleftharpoons B + C
\]

Vanilla Ice wants to know, “What happens if, as the initial state progresses, you keep supplying A and pulling B and C away?” …

http://chemwiki.ucdavis.edu/Physical_Chemistry/Equilibria/Le_Chatelier%27s_Principle/Ice_Tables

http://buzzworthy.mtv.com/2012/11/14/justin-bieber-vanilla-ice-photo/
… Le Chatelier’s Principle keeps the reaction going…

\[ \rightarrow A \leftrightarrow B + C \rightarrow \]

… but for how long? …
... Le Chatelier’s Principle keeps the reaction going...

\[ \rightarrow A \rightleftharpoons B + C \rightarrow \]

... but for how long? ...

\[ M_1 \rightarrow A \rightleftharpoons B + C \rightarrow M_2 \]

... as long as the supply in and the flow out is constant...

... and in electrochemical systems, as long as a constant potential bias is applied!
Le Chatelier’s Principle keeps the reaction going…

\[ \rightarrow A \xleftrightarrow{} B + C \rightarrow \]

… but for how long? …

\[ M_1 \rightarrow A \xleftrightarrow{} B + C \rightarrow M_2 \]

… as long as the supply in and the flow out is constant…

… and in electrochemical systems, as long as a constant potential bias is applied!

In an ideal world, i.e. under certain rare conditions,

\[ \frac{\partial c_A}{\partial t} = \frac{\partial c_B}{\partial t} = \frac{\partial c_C}{\partial t} = 0, \]

and the system is in a steady-state where there is a net flux of species (generation of A and loss of B and C) but the species concentrations in the cell do not change with time.
... when the current is at a steady-state, *the current is constant*, and there is no new capacitive charging!

... for steady-state current, KCL applies... no, not KCL... but **KCL**!
Who cares? …

… when the current is at a steady-state, the current is constant, and there is no new capacitive charging!

Kirchhoff’s Current Law (KCL)

\[ \sum_{k=1}^{n} I_k = 0 \]


... for steady-state current, KCL applies... no, not KCI... but KCL!
But KCL applies to the *entire circuit*, including in the potentiostat!
(when the current flow, i.e. due motion of charges, is at steady-state)

... hey, what are those minus signs at the bottom? ...
But KCL applies to the *entire circuit*, including in the potentiostat! (when the current flow, i.e. due motion of charges, is at steady-state)

... hey, what are those minus signs at the bottom? ...

\[ I \]

\[ M_1 \rightarrow A \leftrightarrow B + C \rightarrow M_2 \]

... hey, what are those minus signs at the bottom? ...

**Migrating/Drifting Ions!**

... we’ll get to this shortly
Back to the first flux term… Diffusion…

**Diffusion coefficient** \((D, \text{ cm}^2 \text{ s}^{-1})\) – “proportionality constant relating the flux of [the] amount of [an entity to its] concentration gradient…” (IUPAC Gold Book)

**Fick’s first law of steady-state Diffusion:** \(N_z = -D_z \frac{dc}{dz}\), in 1D

Do the units of \(D\) make sense? \(N_z\) (mol cm\(^{-2}\) s\(^{-1}\), as \(xy\)) = …

![Diagram of concentration gradient and flux](image)

**Adolf Eugen Fick** (1829–1901)

from Wiki
Diffusion coefficient \((D, \text{cm}^2 \text{s}^{-1})\) – “proportionality constant relating the flux of [the] amount of [an entity to its] concentration gradient…” (IUPAC Gold Book)

**Fick’s first law of steady-state Diffusion:** \(N_z = -D_z \frac{dc}{dz}\), in 1D

Do the units of \(D\) make sense?

\[N_z \text{ (mol cm}^{-2} \text{ s}^{-1}, \text{ as } xy) = D_z \cdot \frac{dc}{dz} \text{ (mol cm}^{-3} \text{ cm}^{-1}, \text{ as } xyz z)\]

\[N_z \text{ (mol cm}^{-2} \text{ s}^{-1}, \text{ as } xy) = D_z \cdot \text{ (mol cm}^{-4}, \text{ as } xyz z)\]
Diffusion coefficient \((D, \text{ cm}^2 \text{ s}^{-1})\) – “proportionality constant relating the flux of [the] amount of [an entity to its] concentration gradient…” (IUPAC Gold Book)

Fick’s first law of **steady-state Diffusion**: \(N_z = -D_z \frac{dc}{dz}\), in 1D

Do the units of \(D\) make sense?

\[
N_z (\text{mol cm}^{-2} \text{ s}^{-1}, \text{ as } xy) = D_z \cdot \frac{dc}{dz} (\text{mol cm}^{-3} \text{ cm}^{-1}, \text{ as } xyz z)
\]

\[
(\text{mol cm}^{-2} \text{ s}^{-1}, \text{ as } xy) = D_z \cdot (\text{mol cm}^{-4}, \text{ as } xyzz)
\]

Therefore, \(D_z\) is has units of \(\text{cm}^2 \text{ s}^{-1}\)… but as \(zz\)…

Huh? \(zz\)? \(z^2\)? What? …

**Adolf Eugen Fick**

(1829–1901)

from Wiki
… well, that must have been incorrect (it’s not!)… anyway, let’s try this again… Grab a beverage and let’s go on a (random) walk!

… Flashback! Pascal’s triangle! …

---

**Figure 4.4.2** (a) Probability distribution for a one-dimensional random walk over zero to four time units. The number printed over each allowed arrival point is the number of paths to that point. (b) Bar graph showing distribution at $t = 4\tau$. At this time, probability of being at $x = 0$ is $6/16$, at $x = \pm 2\ell$ is $4/16$, and at $x = \pm 4\ell$ is $1/16$. From B&F
... well, that must have been incorrect (it’s not!)… anyway, let’s try this again… Grab a beverage and let’s go on a (random) walk!

Figure 4.4.2 (a) Probability distribution for a one-dimensional random walk over zero to four time units. The number printed over each allowed arrival point is the number of paths to that point. (b) Bar graph showing distribution at $t = 4\tau$. At this time, probability of being at $x = 0$ is 6/16, at $x = \pm 2l$ is 4/16, and at $x = \pm 4l$ is 1/16.

From B&F
… well, that must have been incorrect (it’s not!)… anyway, let’s try this again… Grab a beverage and let’s go on a (random) walk!

\[ \overline{\Delta^2} = ml^2 = \frac{t}{\tau}l^2 = 2Dt \]

mean square displacement (variance)

Figure 4.4.2 (a) Probability distribution for a one-dimensional random walk over zero to four time units. The number printed over each allowed arrival point is the number of paths to that point. (b) Bar graph showing distribution at \( t = 4\tau \). At this time, probability of being at \( x = 0 \) is 6/16, at \( x = \pm 2l \) is 4/16, and at \( x = \pm 4l \) is 1/16.

From B&F
... well, that must have been incorrect (it's not!)... anyway, let's try this again... Grab a beverage and let's go on a (random) walk!

\[
\frac{\Delta^2}{m} = l^2 = \frac{t}{\tau} l^2 = 2Dt
\]

Recall, \( D \) is has units of cm² s⁻¹, as \( z \).

Figure 4.4.2 (a) Probability distribution for a one-dimensional random walk over zero to four time units. The number printed over each allowed arrival point is the number of paths to that point. (b) Bar graph showing distribution at \( t = 4\tau \). At this time, probability of being at \( x = 0 \) is 6/16, at \( x = \pm 2l \) is 4/16, and at \( x = \pm 4l \) is 1/16.

From B&F
... well, that must have been incorrect (it’s not!)... anyway, let’s try this again... Grab a beverage and let’s go on a (random) walk!

$$\overline{\Delta^2} = ml^2 = \frac{t}{\tau}l^2 = 2Dt$$

mean square displacement (variance)

Recall, $D_z$ is has units of cm$^2$ s$^{-1}$, as $zz$

**Figure 4.4.2** (a) Probability distribution for a one-dimensional random walk over zero to four time units. The number printed over each allowed arrival point is the number of paths to that point. (b) Bar graph showing distribution at $t = 4\tau$. At this time, probability of being at $x = 0$ is 6/16, at $x = \pm 2l$ is 4/16, and at $x = \pm 4l$ is 1/16.

$m$ is just the number

$\tau$ is step time

$l$ is step length

$$\Delta = \sqrt{(2d)Dt}, \text{ where } d \text{ is the dimension}$$

root mean square (rms) displacement (standard deviation)
... so how far do species diffuse in electrochemistry in 1D?

<table>
<thead>
<tr>
<th>D</th>
<th>$\bar{\Delta}^*$ =</th>
</tr>
</thead>
<tbody>
<tr>
<td>1D</td>
<td>$\sqrt{2Dt}$</td>
</tr>
<tr>
<td>2D</td>
<td>$\sqrt{4Dt}$</td>
</tr>
<tr>
<td>3D</td>
<td>$\sqrt{6Dt}$</td>
</tr>
</tbody>
</table>

*the rms displacement

From a...

... plane

... wire, line, tube

... point, sphere, disk

$\bar{\Delta}^* = \sqrt{(2d)Dt}$

$\bar{\Delta} = \sqrt{(2d)Dt}$, where $d$ is the dimension

A characteristic "diffusion length"

Root mean square (rms) displacement (standard deviation)
… so how far do species diffuse in electrochemistry in 1D?

Given \( D = 5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1} \) (but memorize \( \sim 10^{-5} \text{ cm}^2 \text{ s}^{-1} \)),

\[
\bar{\Delta} = \sqrt{(2d)Dt}, \text{ where } d \text{ is the dimension}
\]

<table>
<thead>
<tr>
<th>time</th>
<th>( \bar{\Delta} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 ms</td>
<td>1 ( \mu \text{m} )</td>
</tr>
<tr>
<td>0.1 s</td>
<td>10 ( \mu \text{m} )</td>
</tr>
<tr>
<td>10 s</td>
<td>0.1 \text{ mm}</td>
</tr>
<tr>
<td>16.7 min</td>
<td>1 \text{ mm}</td>
</tr>
<tr>
<td>1.157 day</td>
<td>1 \text{ cm}</td>
</tr>
<tr>
<td>0.32 year</td>
<td>10 \text{ cm} \approx 3.9&quot;</td>
</tr>
</tbody>
</table>
... what are typical values for diffusion coefficients, for species in electrochemistry?

<table>
<thead>
<tr>
<th>Cation</th>
<th>$D$ (x 10^{-5} \text{ cm}^2/\text{s})</th>
<th>Anion</th>
<th>$D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$^+$</td>
<td>9.31</td>
<td>OH$^-$</td>
<td>5.28</td>
</tr>
<tr>
<td>Li$^+$</td>
<td>1.03</td>
<td>F$^-$</td>
<td>1.47</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>1.33</td>
<td>Cl$^-$</td>
<td>2.03</td>
</tr>
<tr>
<td>K$^+$</td>
<td>1.96</td>
<td>Br$^-$</td>
<td>2.08</td>
</tr>
<tr>
<td>Rb$^+$</td>
<td>2.07</td>
<td>I$^-$</td>
<td>2.05</td>
</tr>
<tr>
<td>Cs$^+$</td>
<td>2.06</td>
<td>NO$_3^-$</td>
<td>1.90</td>
</tr>
<tr>
<td>Ag$^+$</td>
<td>1.65</td>
<td>CH$_3$COO$^-$</td>
<td>1.09</td>
</tr>
<tr>
<td>NH$_4^+$</td>
<td>1.96</td>
<td>CH$_3$CH$_2$COO$^-$</td>
<td>0.95</td>
</tr>
<tr>
<td>N(C$_4$H$_9$)$_4^+$</td>
<td>0.52</td>
<td>B(C$_5$H$_5$)$_4^-$</td>
<td>0.53</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>0.79</td>
<td>SO$_4^{2-}$</td>
<td>1.06</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>0.71</td>
<td>CO$_3^{2-}$</td>
<td>0.92</td>
</tr>
<tr>
<td>La$^{3+}$</td>
<td>0.62</td>
<td>Fe(CN)$_6^{3-}$</td>
<td>0.98</td>
</tr>
</tbody>
</table>

"Diffusion: Mass Transfer in Fluid Systems," 2013, by E. L. Cussler

* on the order of 10^{-6} \text{ cm}^2/\text{s} for molecules
* on the order of 10^{-7} \text{ cm}^2/\text{s} for proteins

\[ \Delta = \sqrt{(2d)Dt}, \text{ where } d \text{ is the dimension} \]
... what are typical values for diffusion coefficients, for species in electrochemistry?

**Table 6.1-1 Diffusion coefficients of ions in water at 25 °C**

<table>
<thead>
<tr>
<th>Cation</th>
<th>Anion</th>
<th>$D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H^+$</td>
<td>$OH^-$</td>
<td>9.31 x 10^{-5} cm$^2$/s</td>
</tr>
<tr>
<td>$Li^+$</td>
<td>$F^-$</td>
<td>1.03</td>
</tr>
<tr>
<td>$Na^+$</td>
<td>$Cl^-$</td>
<td>1.33</td>
</tr>
<tr>
<td>$K^+$</td>
<td>$Br^-$</td>
<td>1.96</td>
</tr>
<tr>
<td>$Rb^+$</td>
<td>$I^-$</td>
<td>2.07</td>
</tr>
<tr>
<td>$Cs^+$</td>
<td>$NO_3^-$</td>
<td>2.06</td>
</tr>
<tr>
<td>$Ag^+$</td>
<td>$CH_3COO^-$</td>
<td>2.06</td>
</tr>
<tr>
<td>$NH_4^+$</td>
<td>$CH_3CH_2COO^-$</td>
<td>1.96</td>
</tr>
<tr>
<td>$N(C_4H_9)_4^+$</td>
<td>$B(C_5H_5)_4^-$</td>
<td>0.52</td>
</tr>
<tr>
<td>$Ca^{2+}$</td>
<td>$SO_4^{2-}$</td>
<td>0.79</td>
</tr>
<tr>
<td>$Mg^{2+}$</td>
<td>$CO_3^{2-}$</td>
<td>0.71</td>
</tr>
<tr>
<td>$La^{3+}$</td>
<td>$Fe(CN)_6^{3-}$</td>
<td>0.62</td>
</tr>
</tbody>
</table>

Why are both so... slow (for example)?

* on the order of $10^{-6}$ cm$^2$/s for molecules
* on the order of $10^{-7}$ cm$^2$/s for proteins

\[
\bar{\Delta} = \sqrt{(2d)Dt}, \text{ where } d \text{ is the dimension}
\]

“Diffusion: Mass Transfer in Fluid Systems,” 2013, by E. L. Cussler

A characteristic "diffusion length" (rms) displacement
… what are typical values for diffusion coefficients, for species in electrochemistry?

<table>
<thead>
<tr>
<th>Cation</th>
<th>$D$ (x $10^{-5}$ cm$^2$/s)</th>
<th>Anion</th>
<th>$D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$^+$</td>
<td>9.31</td>
<td>OH$^-$</td>
<td>5.28</td>
</tr>
<tr>
<td>Li$^+$</td>
<td>1.03</td>
<td>F$^-$</td>
<td>1.47</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>1.33</td>
<td>Cl$^-$</td>
<td>2.03</td>
</tr>
<tr>
<td>K$^+$</td>
<td>1.96</td>
<td>Br$^-$</td>
<td>2.08</td>
</tr>
<tr>
<td>Rb$^+$</td>
<td>2.07</td>
<td>I$^-$</td>
<td>2.05</td>
</tr>
<tr>
<td>Cs$^+$</td>
<td>2.06</td>
<td>NO$_3^-$</td>
<td>1.90</td>
</tr>
<tr>
<td>Ag$^+$</td>
<td>1.65</td>
<td>CH$_3$COO$^-$</td>
<td>1.09</td>
</tr>
<tr>
<td>NH$_4^+$</td>
<td>1.96</td>
<td>CH$_3$CH$_2$COO$^-$</td>
<td>0.95</td>
</tr>
<tr>
<td>N(C$_4$H$_9$)$_4^+$</td>
<td>0.52</td>
<td>B(C$_5$H$_5$)$_4^-$</td>
<td>0.53</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>0.79</td>
<td>SO$_4^{2-}$</td>
<td>1.06</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>0.71</td>
<td>CO$_3^{3-}$</td>
<td>0.92</td>
</tr>
<tr>
<td>La$^{3+}$</td>
<td>0.62</td>
<td>Fe(CN)$_6^{3-}$</td>
<td>0.98</td>
</tr>
</tbody>
</table>

Why are both so… fast?

Why are both so… slow (for example)?

* on the order of $10^{-6}$ cm$^2$/s for molecules
* on the order of $10^{-7}$ cm$^2$/s for proteins

“Diffusion: Mass Transfer in Fluid Systems,” 2013, by E. L. Cussler

A characteristic "diffusion length"

$$\overline{\Delta} = \sqrt{(2d)Dt},$$ where $d$ is the dimension

root mean square (rms) displacement (standard deviation)
Proton (and hydroxide) ions do not diffuse by normal thermal or Brownian motion… they hop between molecules… by a **Grotthuss mechanism**

\[
\begin{align*}
D(H^+) &= 9.31 \times 10^{-5} \text{ cm}^2 \text{s}^{-1} \\
D(OH^-) &= 5.28 \times 10^{-5} \text{ cm}^2 \text{s}^{-1}
\end{align*}
\]

http://www.snipview.com/q/Grotthuss%20mechanism

---

**Chemist**

Theodor von Grotthuss
(1785–1822)

from Wiki

---

a "cartoon"
Proton (and hydroxide) ions do not diffuse by normal thermal or Brownian motion… they hop between molecules… by a **Grotthuss mechanism**

\[
D(H^+) = 9.31 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \\
D(OH^-) = 5.28 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}
\]

**Theodor von Grotthuss** (1785–1822)

from Wiki

http://www.snipview.com/q/Grotthuss%20mechanism
Proton transfer is enabled by an additional O–O bond contraction, not required in H$_5$O$_2^+$. This explains why the activation energy for hydroxide mobility is larger than that of proton mobility by about 0.5 kcal/mol. The transfer cycle is terminated by hydrogen-bond formation to the other oxygen center. Available experimental data, and most of the computational results, can be rationalized in the framework of the above model. © 2000 Elsevier Science B.V. All rights reserved.


**ABSTRACT:** The diffusion of hydronium (H$_3$O$^+$) and hydroxide (OH$^-$) ions is one of the most intriguing topics in aqueous chemistry. It is considered that these ions in aqueous solutions move via sequential proton transfer events, known as the Grotthuss mechanisms. Here, we present an experimental study of the diffusion and H/D exchange of hydronium and hydroxide ions in amorphous solid water (ASW) at 140–180 K by using low-energy sputtering (LES) and temperature-programmed desorption (TPD) measurements. The study shows that the two species transport in ASW via fundamentally different molecular mechanisms. Whereas hydronium ions migrate via efficient proton transfer, hydroxide ions move via Brownian molecular diffusion without proton transfer. The molecular hydroxide diffusion in ASW is in stark contrast to the current view of the hydroxide diffusion mechanism in aqueous solution, which involves proton transfer.
... remember this... but now let's say the walker is charged...

"Captain e^{-}\""

Figure 4.4.2 (a) Probability distribution for a one-dimensional random walk over zero to four time units. The number printed over each allowed arrival point is the number of paths to that point. (b) Bar graph showing distribution at t = 4\tau. At this time, probability of being at x = 0 is 6/16, at x = \pm 2l is 4/16, and at x = \pm 4l is 1/16.

... Flashback! Pascal's triangle! ...
... what if we applied an external field to this scenario...

Figure 4.4.2  (a) Probability distribution for a one-dimensional random walk over zero to four time units. The number printed over each allowed arrival point is the number of paths to that point. (b) Bar graph showing distribution at $t = 4\tau$. At this time, probability of being at $x = 0$ is $6/16$, at $x = \pm 2\tau$ is $4/16$, and at $x = \pm 4\tau$ is $1/16$.

... Flashback! Pascal's triangle! ...
… what if we applied an external field to this scenario…
… then the random walk would no longer be quite so random!

… welcome to the concept of ionic drift

Figure 4.4.2  (a) Probability distribution for a one-dimensional random walk over zero to four time units. The number printed over each allowed arrival point is the number of paths to that point. (b) Bar graph showing distribution at $t = 4\tau$. At this time, probability of being at $x = 0$ is 6/16, at $x = \pm 2\ell$ is 4/16, and at $x = \pm 4\ell$ is 1/16.

… Flashback! Pascal’s triangle! …
Diffusion coefficient \((D, \text{ cm}^2 \text{s}^{-1})\) – “proportionality constant relating the flux of [the] amount of [an entity to its] concentration gradient…” (IUPAC Gold Book)

**Fick’s first law of steady-state Diffusion:** \(N_z = -D_z \frac{dc}{dz}\), in 1D

Mobility \((\mu, \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})\) – “the limiting velocity of an ion in an electric field of unit strength” (B&F, pg. 66)… or a proportionality constant relating the velocity of an ion to the electric field strength

… start with **Newton’s second law of motion:** \(F = m \cdot a\)
Diffusion coefficient \((D, \text{ cm}^2 \text{ s}^{-1})\) – “proportionality constant relating the flux of [the] amount of [an entity to its] concentration gradient…” (IUPAC Gold Book)

**Fick’s first law of steady-state Diffusion:** \(N_z = -D_z \frac{dc}{dz}\), in 1D

Mobility \((\mu, \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})\) – “the limiting velocity of an ion in an electric field of unit strength” (B&F, pg. 66)… or a proportionality constant relating the velocity of an ion to the electric field strength

… start with **Newton’s second law of motion:** \(F = m \cdot a\)

… \(|z|eE = m \cdot \frac{v_d}{\tau}\), with \(e\), elementary charge (C),

\(E,\) electric field (V cm\(^{-1}\)),
\(v_d,\) average drift velocity (cm s\(^{-1}\)),
\(\tau,\) mean time (s) to reset drift motion through collisions (i.e. \(v = 0\))
Diffusion coefficient \((D, \text{ cm}^2 \text{s}^{-1})\) – “proportionality constant relating the flux of [the] amount of [an entity to its] concentration gradient…” (IUPAC Gold Book)

**Fick’s first law of steady-state Diffusion:** \(N_z = -D_z \frac{dc}{dz}\), in 1D

Mobility \((\mu, \text{ cm}^2 \text{V}^{-1} \text{s}^{-1})\) – “the limiting velocity of an ion in an electric field of unit strength” (B&F, pg. 66)… or a proportionality constant relating the velocity of an ion to the electric field strength

… start with **Newton’s second law of motion:** \(F = m \cdot a\)

\( |z|eE = m \cdot \frac{v_d}{\tau} \), with \(e\), elementary charge (C),

\(E\), electric field (V cm\(^{-1}\)),
\(v_d\), average drift velocity (cm s\(^{-1}\)),
\(\tau\), mean time (s) to reset drift motion through collisions (i.e. \(v = 0\))

Because \(v_{d-z} = \mu_z \cdot E_z\), this means that \(\mu = |z|e \frac{\tau}{m}\)
Diffusion coefficient \((D, \text{ cm}^2 \text{ s}^{-1})\) – “proportionality constant relating the flux of [the] amount of [an entity to its] concentration gradient…” (IUPAC Gold Book)

**Fick’s first law of steady-state Diffusion**: \(N_z = -D_z \frac{dc}{dz}\), in 1D

Mobility \((\mu, \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})\) – “the limiting velocity of an ion in an electric field of unit strength” (B&F, pg. 66)… or a proportionality constant relating the velocity of an ion to the electric field strength

… start with **Newton’s second law of motion**: \(F = m \cdot a\)

\[|z|eE = m \cdot \frac{v_d}{\tau},\] with \(e\), elementary charge (C),

\(E\), electric field (V cm\(^{-1}\))

\(v_d\), average drift velocity (cm s\(^{-1}\))

\(\tau\), mean time (s) to reset drift motion through collisions (i.e. \(v = 0\))

Because \(v_{d-z} = \mu_z \cdot E_z\), this means that \(\mu = |z|e \frac{\tau}{m}\)

… and the units of mobility are correct … \((\text{cm s}^{-1}) = \mu \cdot (\text{V cm}^{-1})\)
... and another formula for ionic mobility, $\mu_i$

the mobility is defined from **Stokes' law** by the **Stokes–Einstein equation** based on the balance of forces acting on a particle, with charge, $ze$, and moving in an electric field, $E$:

$$6\pi\eta rv \leftrightarrow ze \Rightarrow |z_i| eE$$

Mathematician, Physicist, Politician, and Theologian

Sir George Gabriel Stokes (1819–1903)

Physicist & Philosopher

Albert Einstein (1879–1955)

from Wiki
the mobility is defined from **Stokes’ law** by the **Stokes–Einstein equation** based on the balance of forces acting on a particle, with charge, \( ze \), and moving in an electric field, \( E \):

\[
\mu_i = \frac{\nu}{E} = \frac{|z_i|e}{6\pi \eta r}
\]

\( 6\pi \eta rv \) \( \rightarrow \) \( z_e \) \( \rightarrow \) \( |z_i|eE \)

- **Viscous drag**
- **Electrophoretic force**
- **Particle velocity**

---

Mathematician, Physicist, Politician, and Theologian

Sir George Gabriel Stokes (1819–1903)

Physicist & Philosopher

Albert Einstein (1879–1955)
Diffusion coefficient \((D, \text{ cm}^2 \text{ s}^{-1})\) – “proportionality constant relating the flux of [the] amount of [an entity to its] concentration gradient…” (IUPAC Gold Book)

**Fick’s first law of steady-state Diffusion:** \(N_z = -D_z \frac{dc}{dz}\), in 1D

Mobility \((\mu, \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})\) – “the limiting velocity of an ion in an electric field of unit strength” (B&F, pg. 66)… or a proportionality constant relating the velocity of an ion to the electric field strength

**Newton’s second law of motion:** \(F = m \cdot a, \nu_d = \mu \cdot E\)

**Stokes’ law:** \(F = |z|eE = 6\pi\eta r\nu_d\), and so by solving \(\mu = \frac{\nu_d}{E}\) above, one gets \(\mu = \frac{|z|e}{6\pi\eta r}\) which gives a physical meaning to the mobility, with \(\eta\) (dynamic viscosity of the medium) and \(r\) (radius of the spherical ion)

Mathematician, Physicist, Politician, and Theologian

Sir George Gabriel Stokes (1819–1903) from Wiki
Diffusion coefficient \((D, \text{ cm}^2 \text{ s}^{-1})\) – “proportionality constant relating the flux of [the] amount of [an entity to its] concentration gradient…” (IUPAC Gold Book)

Fick’s first law of steady-state Diffusion: \(N_z = -D_z \frac{dc}{dz}\), in 1D

Mobility \((\mu, \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})\) – “the limiting velocity of an ion in an electric field of unit strength” (B&F, pg. 66)… or a proportionality constant relating the velocity of an ion to the electric field strength

Newton’s second law of motion: \(F = m \cdot a, \; v_d = \mu \cdot E\)

… and a very important point is that these two parameters, \(D\) and \(\mu\), are related!
Diffusion coefficient \((D, \text{cm}^2 \text{s}^{-1})\) – “proportionality constant relating the flux of [the] amount of [an entity to its] concentration gradient…” (IUPAC Gold Book)

**Fick’s first law of steady-state Diffusion:** \(N_z = -D_z \frac{dc}{dz}\), in 1D

Mobility \((\mu, \text{cm}^2 \text{V}^{-1} \text{s}^{-1})\) – “the limiting velocity of an ion in an electric field of unit strength” (B&F, pg. 66)… or a proportionality constant relating the velocity of an ion to the electric field strength

**Newton’s second law of motion:** \(F = m \cdot a, v_d = \mu \cdot E\)

… and a very important point is that these two parameters, \(D\) and \(\mu\), are related!

… Einstein–Smoluchowski equation,

\[
\mu_i = \frac{|z_i| F D_i}{RT}
\]
Diffusion coefficient \((D, \text{ cm}^2 \text{ s}^{-1})\) – “proportionality constant relating the flux of [the] amount of [an entity to its] concentration gradient…” (IUPAC Gold Book)

**Fick’s first law of steady-state Diffusion:** \(N_z = -D_z \frac{dc}{dz}\), in 1D

Mobility \((\mu, \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})\) – “the limiting velocity of an ion in an electric field of unit strength” (B&F, pg. 66)… or a proportionality constant relating the velocity of an ion to the electric field strength

**Newton’s second law of motion:** \(F = m \cdot a, v_d = \mu \cdot E\)

… and a very important point is that these two parameters, \(D\) and \(\mu\), are related!

… Einstein–Smoluchowski equation,

\[
\mu_i = \frac{|z_i|FD_i}{RT}
\]

… and what is the value of \(\frac{RT}{F}\)?
Diffusion coefficient \((D, \text{ cm}^2 \text{ s}^{-1})\) – “proportionality constant relating the flux of [the] amount of [an entity to its] concentration gradient…” (IUPAC Gold Book)

**Fick’s first law of steady-state Diffusion:** \(N_z = -D_z \frac{dc}{dz}\), in 1D

Mobility \((\mu, \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})\) – “the limiting velocity of an ion in an electric field of unit strength” (B&F, pg. 66)… or a proportionality constant relating the velocity of an ion to the electric field strength

**Newton’s second law of motion:** \(F = m \cdot a, v_d = \mu \cdot E\)

…and a very important point is that these two parameters, \(D\) and \(\mu\), are related!

… Einstein–Smoluchowski equation,

\[
\mu_i = \frac{|z_i| F D_i}{RT}
\]

…and what is the value of \(\frac{RT}{F}\)? **25.7 mV**
... and now lastly, a simplified (cleaner) Nernst–Planck equation...

\[
J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} - \frac{z_i F}{RT} D_i C_i \frac{\partial \phi(x)}{\partial x} + C_i \nu(x)
\]
From before, for one species the total flux in one-dimension is

\[ N = -\frac{Dc}{RT} \cdot \frac{d\mu}{dx} + cv, \ldots \{\text{several math steps from before}\} \]

\[ N = -D \cdot \frac{dc}{dx} - \frac{zFD}{RT}c \cdot \frac{d\phi}{dx} + cv \ldots \]

\[ J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} - \frac{z_iF}{RT} D_i C_i \frac{\partial \phi(x)}{\partial x} + C_i \nu(x) \]
… and now lastly, a simplified (cleaner) Nernst–Planck equation...

From before, for one species the total flux in one-dimension is

\[ N = - \frac{Dc}{RT} \cdot \frac{d\mu}{dx} + cv, \ldots \]  

\[ \text{\{several math steps from before\}} \]

\[ N = -D \cdot \frac{dc}{dx} - \frac{zFD}{RT}c \cdot \frac{d\phi}{dx} + cv \ldots \]

… which can also be written using the E–S equation

\[ \mu_i = \frac{|z_i|FD_i}{RT} \]

\[ D_i = \frac{RT \mu_i}{|z_i|F} \]

B&F, 4.2.2

\[ J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} - \frac{z_iF}{RT} D_i C_i \frac{\partial \phi(x)}{\partial x} + C_i \nu(x) \]
... and now lastly, a simplified (cleaner) Nernst–Planck equation...

From before, **for one species** the total flux in one-dimension is

\[ N = -\frac{Dc}{RT} \cdot \frac{d\mu}{dx} + cv, \ldots \{\text{several math steps from before}\} \]

\[ N = -D \cdot \frac{dc}{dx} - \frac{zFD}{RT} c \cdot \frac{d\phi}{dx} + cv \ldots \]

... which can also be written using the E–S equation

\[ N = -D \cdot \frac{dc}{dx} - \left| \frac{z_i}{z_i} \right| \mu c \cdot \frac{d\phi}{dx} + cv \]

\[ \mu_i = \frac{|z_i|F D_i}{RT} \]

\[ D_i = \frac{RT \mu_i}{|z_i|F} \]

B&F, 4.2.2

\[ J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} - \frac{z_i F}{RT} D_i C_i \frac{\partial \phi(x)}{\partial x} + C_i v(x) \]
... and now lastly, a simplified (cleaner) Nernst–Planck equation...

From before, **for one species** the total flux in one-dimension is

\[ N = -\frac{Dc}{RT} \cdot \frac{d\mu}{dx} + cv, \ldots \{\text{several math steps from before}\} \]

\[ N = -D \cdot \frac{dc}{dx} - \frac{zFD}{RT}c \cdot \frac{d\phi}{dx} + cv \ldots \]

... which can also be written using the E–S equation

\[ \mu_i = \frac{|z_i|FD_i}{RT} \]

\[ D_i = \frac{RT\mu_i}{|z_i|F} \]

As again, recall that the current density can be simplified even further, in the absence of convection...

\[ J_i(x) = \pm \sigma_i \frac{d\mu_i}{dx} \]

B&F, 4.2.2

\[ J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} - \frac{z_i F}{RT} D_i C_i \frac{\partial \phi(x)}{\partial x} + C_i \nu(x) \]
… some textbooks (Bockris) initially define the migration term in terms of mobility based on straightforward physical reasoning…
… some textbooks (Bockris) initially define the migration term in terms of mobility based on straightforward physical reasoning…

… then, the Nernst–Planck equation for an anion can be defined as…

\[ N = -D \cdot \frac{dc}{dx} + \mu c \cdot \frac{d\phi}{dx} + cv \]

… and the E–S equation can be derived using this version…
... then, the Nernst–Planck equation for an anion can be defined as...

\[ N = -D \frac{dc}{dx} + \mu c \cdot \frac{d\phi}{dx} + cv \]

... and the E–S equation can be derived using this version...

... evaluate the condition where the net flux is zero in a quiescent solution, meaning transport due to Brownian motion and that from the force of an electric field cancel each other out...

\[ 0 = -D \frac{dc}{dx} + \mu c \cdot \frac{d\phi}{dx} + cv \]

Bockris & Reddy, Fig. 4.62
... then, the Nernst–Planck equation for an anion can be defined as...

\[ N = -D \cdot \frac{dc}{dx} + \mu c \cdot \frac{d\phi}{dx} + cv \]

... and the E–S equation can be derived using this version...

... evaluate the condition where the net flux is zero in a quiescent solution, meaning transport due to Brownian motion and that from the force of an electric field cancel each other out...

\[ 0 = -D \cdot \frac{dc}{dx} + \mu c \cdot \frac{d\phi}{dx} + cv \]

\[ D \cdot \frac{dc}{dx} = \mu c \cdot \frac{d\phi}{dx}, \text{ and using the “Boltzmann law,” } c = c_0 e^{-\frac{U}{RT}}, \]
... then, the Nernst–Planck equation for an anion can be defined as:

\[ N = -D \cdot \frac{dc}{dx} + \mu c \cdot \frac{d\phi}{dx} + cv \]

... and the E–S equation can be derived using this version...

... evaluate the condition where the net flux is zero in a quiescent solution, meaning transport due to Brownian motion and that from the force of an electric field cancel each other out...

\[ 0 = -D \cdot \frac{dc}{dx} + \mu c \cdot \frac{d\phi}{dx} + cv \]

\[ D \cdot \frac{dc}{dx} = \mu c \cdot \frac{d\phi}{dx} \]

and using the “Boltzmann law,” \( c = c_0 e^{-\frac{U}{RT}} \), \( D \left( -\frac{1}{RT} c_0 e^{-\frac{U}{RT}} \cdot \frac{dU}{dx} \right) = \mu \left( c_0 e^{-\frac{U}{RT}} \right) \cdot \frac{d\phi}{dx} \)

\[ D \left( -\frac{1}{RT} \cdot \frac{dU}{dx} \right) = \mu \cdot \frac{d\phi}{dx} \]
... then, the Nernst–Planck equation for an anion can be defined as...

\[ N = -D \cdot \frac{dc}{dx} + \mu c \cdot \frac{d\phi}{dx} + cv \]

... and the E–S equation can be derived using this version...

... evaluate the condition where the net flux is zero in a quiescent solution, meaning transport due to Brownian motion and that from the force of an electric field cancel each other out...

\[ 0 = -D \cdot \frac{dc}{dx} + \mu c \cdot \frac{d\phi}{dx} + cv \]

\[ D \cdot \frac{dc}{dx} = \mu c \cdot \frac{d\phi}{dx}, \text{ and using the “Boltzmann law,” } c = c_0 e^{-\frac{U}{RT}}, \]

\[ D \left( -\frac{1}{RT} c_0 e^{-\frac{U}{RT}} \cdot \frac{dU}{dx} \right) = \mu \left( c_0 e^{-\frac{U}{RT}} \right) \cdot \frac{d\phi}{dx} \]

\[ D \left( -\frac{1}{RT} \cdot \frac{dU}{dx} \right) = \mu \cdot \frac{d\phi}{dx}, \text{ and because the electric potential component of the (free) energy is } zF\phi, \text{ then } \frac{dU}{d\phi} = zF, \]

\[ D \left( -\frac{1}{RT} \cdot zF \right) = \mu = \frac{|z|FD}{RT} \ldots \]
… then, the Nernst–Planck equation for an \textit{anion} can be defined as…

\[
N = -D \cdot \frac{dc}{dx} + \mu c \cdot \frac{d\phi}{dx} + cv
\]

… and the E–S equation can be derived using this version…

… evaluate the condition where the net flux is zero in a quiescent solution, meaning transport due to Brownian motion and that from the force of an electric field cancel each other out…

\[
0 = -D \cdot \frac{dc}{dx} + \mu c \cdot \frac{d\phi}{dx} + cv
\]

\[
D \cdot \frac{dc}{dx} = \mu c \cdot \frac{d\phi}{dx}, \text{ and using the "Boltzmann law," } c = c_0 e^{-\frac{U}{RT}},
\]

\[
D \left( -\frac{1}{RT} c_0 e^{-\frac{U}{RT}} \cdot \frac{dU}{dx} \right) = \mu \left( c_0 e^{-\frac{U}{RT}} \right) \cdot \frac{d\phi}{dx}
\]

\[
D \left( -\frac{1}{RT} \cdot \frac{dU}{dx} \right) = \mu \cdot \frac{d\phi}{dx}, \text{ and because the electric potential component of the (free) energy is } zF\phi, \text{ then } \frac{dU}{d\phi} = zF,
\]

\[
D \left( -\frac{1}{RT} \cdot zF \right) = \mu = \frac{|z|FD}{RT} \ldots \text{the Einstein–Smoluchowski eqn.}
\]