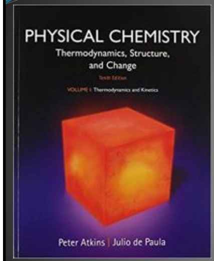

How does the system reach equilibrium?

PHYSICAL CHEMISTRY

I./9 Chemical equilibrium
I./10 Equilibrium electrochemistry

III./24 Molecules in motion – physical processes, non-reactive systems
III./25-27 Reaction rate, mechanism, molecular dynamics of chemical systems – reactive systems
III./28 Processes on solid surfaces
III./29 Dynamic electrochemistry, photochemistry, non-thermal activation

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Molecules in motion

- Different states of matter (different phases) and their properties, similarities and differences
- Transport processes
  - Diffusion: transport of matter
  - Thermal conductivity: transport of energy
  - Viscosity: transport of momentum
- Interpretation of transport processes with the kinetic theory of gases
- Effusion
- Barometric formula

2

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- Week 1:

Properties of gases (overview)

State of matter:	GAS (g)	LIQUID (l)	SOLID (s)
Fixed shape	no	no	yes
Fixed volume	no	yes	yes

An example of phenomenological description.

State of matter:	GAS (g)	LIQUID (l)	SOLID (s)
The particles' potential energy	small	medium	large
kinetic energy	large	medium	small
ordering	no	yes?	yes

An example of (qualitative) interpretation.

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- **Consequence:** the movement of molecules and their macroscopic properties differ significantly in the three phases, but they have many common features.

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Similarities and differences:

- **Diffusion** and **thermal conduction** exist in all three states of matter (all three phases): there is a gradient in c or T which tends to zero with transport on the molecular level (not a macroscopic convection); the equations describing these two processes are similar.
- **Viscosity** exists only in fluid and gas phase, not in crystals.
- **Ion conduction**: can be detected only in electronic force gradient (voltage). Exists only in solutions and melts. In solid phase, there is electronic conduction instead. In gas phase, there is electric discharge.

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Similarities and differences:

- The **pressure**:
  - **In gases**: molecules have large kinetic energy. The moment changes when they collide with the wall. This results in the pressure on all walls of the container (up, down, sides!) This exist without gravity.
  - **In liquids**: there is small kinetic energy, this cannot result in any pressure directly. In a gravity field, the mass of the liquid causes pressure on the bottom of the container which is transported to the side walls by molecular motions.
  - **In solids**: pressure can be measured only on the bottom of the container in gravity field.

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Classifications of systems in a given state of matter:

- free from external forces. Within this:
  - T, p, c are homogeneous (in equilibrium!)
  - T, p, c are inhomogeneous, *e.g.* there is T, p, c or density gradient in the system. In this case, transport processes (heat transport, diffusion, viscosity, convection, mixing, pressure waves) will start to equalize the μ differences.
- In external force field (inhomogeneous pressure, gravity field, electrical field, magnetic field ...)
  - Different processes will start depending on the state of matter: change of V, p, change of shape, flow, density change, electric conduction ...

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Molecules in motion

Again, we start with the simplest systems:

- **Physical changes** are discussed, in which there are no chemical reactions (only transport phenomena, transport processes in non-reactive systems),
- afterwards, we will discuss the **chemical systems** (chemical reactions, reactive systems) – including dynamic electrochemistry.

1. We will formulate the phenomena, measure the phenomenological behavior, write the equations,
2. then explain them using simple models – the motions of molecules.

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Transport phenomena

Phenomenon	gradient	transport
Diffusion	concentration	matter
thermal conduction	temperature	energy
viscosity	velocity	momentum
ionic conduction	electronic potential	charge

- Transport processes can be found in all three phases (with some exceptions – *e.g.* no electrolytic conduction in gases and solids).
- In transport processes, only the molecules are in motion, the system and its macroscopic parts are not. There is no convection or mixing.

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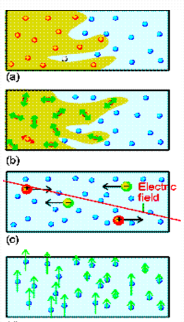
Transport phenomena

- Diffusion:
  - particle transport
- Thermal conduction:
  - energy transport
- Electrolytic conduction:
  - charge transport
- Viscosity:
  - momentum transport



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Transport phenomena

Common concepts in transport phenomena:

- **gradient**: one of the parameters (T, c, E ...) is inhomogeneously distributed in space, at least in one direction.
- **flux**: the quantity of a given property (m, v ...) passing through a given area in a given time interval divided by the area and the duration of the interval. Symbol: J(matter, charge ...).

$$J(\text{matter}) \propto \frac{\mathrm{d}N}{\mathrm{d}z}$$

- N: density of particles (the number of particles per volume)

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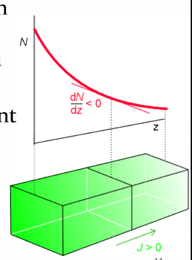
Diffusion: transport of matter (at molecular level)

$$J(\text{matter}) = -D\frac{\mathrm{d}N}{\mathrm{d}z}$$

[J]: $\mathrm{m^{-2}\,s^{-1}}$ flux of matter
[D]: $\mathrm{m^{2}\,s^{-1}}$ diffusion coefficient
[$\mathrm{d}N/\mathrm{d}z$]: $\mathrm{m^{-4}}$ concentration gradient

- **Fick's first law of diffusion**: diffusion will be faster when the concentration varies steeply with position than when the concentration is nearly uniform.
- Different concentrations mean different chemical potentials (since μ depends on c),
- Practical importance: *e.g.* motion of matter in soils.
- *Convection: macroscopic!*



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Thermal conduction: transport of energy

$$J(\text{energy}) = -\kappa\frac{\mathrm{d}T}{\mathrm{d}z}$$

[J]: $\mathrm{J\,m^{-2}\,s^{-1}}$ flux of energy
[κ]: $\mathrm{J\,K^{-1}\,m^{-1}\,s^{-1}}$ coefficient of thermal conductivity
[$\mathrm{d}T/\mathrm{d}z$]: $\mathrm{K\,m^{-1}}$ temperature gradient

- Energy migrates down a temperature gradient.
- The connection between flux and gradient is similar to **Fick's first law of diffusion**.
- Good thermal conductors: metals (Ag, Cu, Au, Al), marble, diamond
- Good thermal insulators: vacuum, CO_2, plastic, wood
- Practical importance: thermal insulation of houses.
- There is **molecular heat conduction**, **macroscopic (convective) heat flow** and **heat radiation**.

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Viscosity: transport of momentum

$$J(\text{momentum})_z = -\eta \frac{\mathrm{d}v_x}{\mathrm{d}z}$$

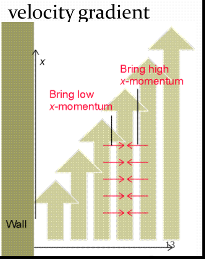
$[J]$: kg m^{-1} s^{-2} flux of momentum

$[\eta]$: kg m^{-1} s^{-1} coefficient of viscosity (or simply 'the viscosity')

1 P (poise) = 0.1 kg m^{-1} s^{-1}

$[\mathrm{d}v_x/\mathrm{d}z]$: s^{-1} velocity gradient

- Because the retarding effect depends on the transfer of the ***x***-component of linear momentum into the layer of interest,
- the viscosity depends on the flux of this ***x***-component in the ***z***-direction.



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Data for gases:

- diffusion coefficients: 10^{-4} m^2 s^{-1}
- coefficients of thermal conductivity: 0.01-0.1 J K^{-1} m^{-1} s^{-1}
- coefficients of viscosity: 1-2×10^{-5} kg m^{-1} s^{-1}

	Density (g cm^{-3})	Diffusion (cm^2 s^{-1})	Viscosity (g cm^{-1} s^{-1})
Gas	10^{-3}	10^{-1}	10^{-4}
Supercritical fluid	10^{-1} – 1 *Liquid-like*	10^{-4} – 10^{-3} *Liquid-like*	10^{-4} – 10^{-3} *Gas-like*
Liquid	1	< 10^{-5}	10^{-2}

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Experimental observations:

- Transport equations, including
- interpretation of various coefficients based on molecular modelling.
- The phenomenological description (the mathematical from of the equations) does not depend on the state of matter, but the particular properties of the system and so the models do.

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Kinetic theory of gases:

- Molecules in the gaseous phase (macroscopic equilibrium).
  - The gas particles (with m mass) move continuously in a straight line with constant speed and
  - they collide. The collisions are perfectly elastic (there is no change in the shape of the molecule).
- The gas molecules have „only" m mass and v velocity, so, momentum (mv) and kinetic energy (1/2 mv^2). Identity, size, shape, structure and orientation do not matter.
- This model is refined for interpreting other phenomena.
- **Real gases:** attraction and repulsion between molecules and the volume of the particles is considered as well) (van der Waals equation).
- Maxwell–Boltzmann distribution (interpretation of E_a).

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Kinetic theory of gases:

The kinetic theory of gases (among others)

- interprets the pressure that the gas exerts on the (relatively small) wall of the container:
  - particles with mass m, speed v and momentum mv collide with the wall elastically (without deformation), the change in momentum (from $+mv$ to $-mv$) results in a force that causes the pressure, which is uniform within the entire volume of the gas.
  $$pV = \frac{1}{3} nMv^2$$
  - In a container filled with a liquid, the pressure is caused by the weight of the liquid that arises with the mass of the particles in interaction with the gravity of the Earth), and not the translational motion of particles. This sort of pressure does not exist in space (gravity = 0), but gases have pressure there as well.

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Kinetic theory of gases - results:

- **Mean free path**: $$\lambda = \frac{k_B T}{\sqrt{2}\sigma p}$$
  - σ: collision cross-section
  - p and T have opposite effects on λ.
- **Mean speed** of a particle with m mass (*i.e.* $M = N_A \cdot m$ molar mass): $$\bar{c} = \left(\frac{8k_B T}{\pi m}\right)^{1/2} = \left(\frac{8RT}{\pi M}\right)^{1/2}$$
  - The mean speed is directly proportional with $T^{1/2}$ and
  - inversely proportional to $M^{1/2}$.
- **Collision frequency**: $$Z_w = \frac{p}{(2\pi m k_B T)^{1/2}}$$
  - Z_w: the number of collisions made by one molecule divided by the time interval during which the collisions are counted

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Effusion – phenomenon, law and interpretation

- **Effusion**: gas slowly escapes through a small hole into an external vacuum (a tire becomes flat slowly if the hole is small *[Vacuum is relative: the essence is the unidirectional diffusion.]*
- **Graham's law of effusion**: the rate of effusion is inversely proportional to the square root of the molar mass (an old determination method for molar mass): $\text{rate of effusion} \propto \frac{1}{\sqrt{M}}$
  - By measuring the mass of the remaining gas, the process can be monitored readily.
  - The rate of effusion can be calculated as the product of the collision frequency (Z_w) and the surface area of the hole (A_o): $\text{rate of effusion} = Z_w A_o = \frac{pA_o}{(2\pi m k_B T)^{1/2}} = \frac{pA_o N_A}{(2\pi MRT)^{1/2}}$

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Effusion – applications

- The pressure in an effusion chamber decreases exponentially:

$$p = p_0 e^{-t/\tau}, \quad \text{where} \quad \tau = \left(\frac{2\pi m}{k_B T}\right)^{1/2} \frac{V}{A_o}$$

- Determination of the vapor pressure of moderately volatile liquids by monitoring the effusion in time: this is important e.g. during the preparation of thin metal coatings by evaporation. The metal is placed into the effusion chamber at high temperature. The evaporation of the metal makes up for the effusion, in time Δt the mass loss Δm is readily measurable: $p = \left(\frac{2\pi RT}{M}\right)^{1/2} \frac{\Delta m}{A_o \Delta t}$

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Inhomogeneity in gas pressure in an external force field:

- In a force field (e.g. gravity field of Earth), the pressure is not uniform (e.g. atmosphere): there is an exponential decrease in pressure with the elevation. This is described by the barometric formula:

$$p = p_0 e^{-\frac{Mgh}{RT}}$$

- The phenomenon can be observed in n an artificial „gravity" field (centrifuge) as well, and the distribution (which depend on the molar mass) can be used in separating different isotopes.

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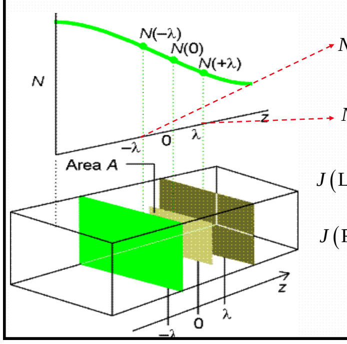
Calculation of the diffusion constant in a gas:



$$N(-\lambda) = N(0) - \lambda\left(\frac{dN}{dz}\right)_0$$

$$N(\lambda) = N(0) + \lambda\left(\frac{dN}{dz}\right)_0$$

$$J(\text{Left} \to \text{Right}) = \frac{N(-\lambda)\cdot\bar{c}}{4}$$

$$J(\text{Right} \to \text{Left}) = -\frac{N(\lambda)\cdot\bar{c}}{4}$$

$$J_z = -\frac{1}{2}\lambda\bar{c}\left(\frac{dN}{dz}\right)_0$$

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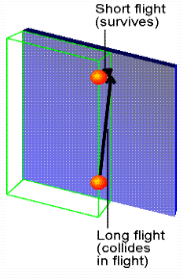
The transport constants from the kinetic theory of gases:



diffusion coefficient:	$D = \frac{1}{3}\lambda\bar{c}$
coefficient of thermal conductivity:	$\kappa = \frac{1}{3}\lambda\bar{c}C_{V,m}[A]$
coefficient of viscosity:	$\eta = \frac{1}{3}\lambda\bar{c}mN$

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More about diffusion:

- The concept of F' **thermodynamic force**: similar to the mechanical force [dw = –F'dx].
- In thermodynamics, the maximum non-expansion work is given by: dw = dμ
- If the chemical potential depends on the spatial coordinate: $dw = d\mu = \left(\frac{\partial \mu}{\partial x}\right)_{p,T} dx$
- Comparing the two equations gives a formula for the thermodynamic force arising from the difference (gradient) in chemical potential: $F' = -\left(\frac{\partial \mu}{\partial x}\right)_{p,T}$

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More about **diffusion**:

- The thermodynamic force for a solute can be given using its activity (concentration): $\mu = \mu^{\ominus} + RT\ln a$
- If the solution is homogeneous: $F' = -RT\left(\frac{\partial \ln a}{\partial x}\right)_{p,T}$
- If the solution is ideal: $a \rightarrow c$ so: $F' = -\frac{RT}{c}\left(\frac{\partial c}{\partial x}\right)_{p,T}$
  - The value of F' can be calculated. Its unit is $\mathrm{N\ mol^{-1}}$.
- Fick's first law of diffusion: $J = -D\left(\frac{\partial c}{\partial x}\right)$
- The J flux is directly proportional to the s drift speed (and the c concentration): $J = sc$
- In this case, using F': $s = \frac{J}{c} = -\frac{D}{c}\left(\frac{\partial c}{\partial x}\right) = \frac{DF'}{RT}$
- So, s or D can be calculated.

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More about **diffusion**:

- For electrolytic conduction (*see later*): $s = \varepsilon u = \frac{\varepsilon z F D}{RT}$
- From this, the **Einstein equation** can be derived: $\boxed{D = \frac{uRT}{zF}}$
- This is the connection between the easily measureable u ion mobility and the D diffusion coefficient (for ions).
- From this, the **Nernst–Einstein equation** can be given:

$$\boxed{\Lambda_m^0 = \frac{F^2}{RT}\left(\nu_+ z_+^2 D_+ + \nu_- z_-^2 D_-\right)}$$

- and the **Stokes–Einstein equation**: $\boxed{D = \frac{k_B T}{6\pi\eta a_{hydr}}}$

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Time and diffusion: **the diffusion equation (Fick's 2nd law)**

- At a given position x, the concentrations change is given as:

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}$$

<u>Some solutions of the diffusion equation</u>:

- An initial value and two boundary conditions are needed:
  - At t = o, the concentration is N_o in the x, y plane
  - No reactions in the system
  - Concentration are always finite.
  - *Sugar at the bottom of the tea cup: diffusion in space*

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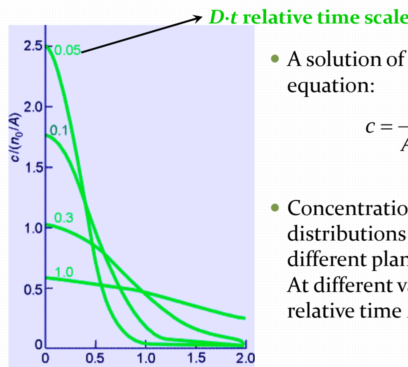

- A solution of the diffusion equation:

$$c = \frac{n_0 e^{-\frac{x^2}{4Dt}}}{A(\pi D t)^{1/2}}$$

- Concentration distributions above different planes – At different values of relative time $D \cdot t$

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Extension of Fick's 2nd law:

- Diffusion only:

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}$$

- <u>Convection</u> and diffusion:

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} - v_z\frac{\partial c}{\partial z}$$

- <u>Chemical reaction</u>, convection and diffusion:

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} - v_z\frac{\partial c}{\partial z} - kc$$

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