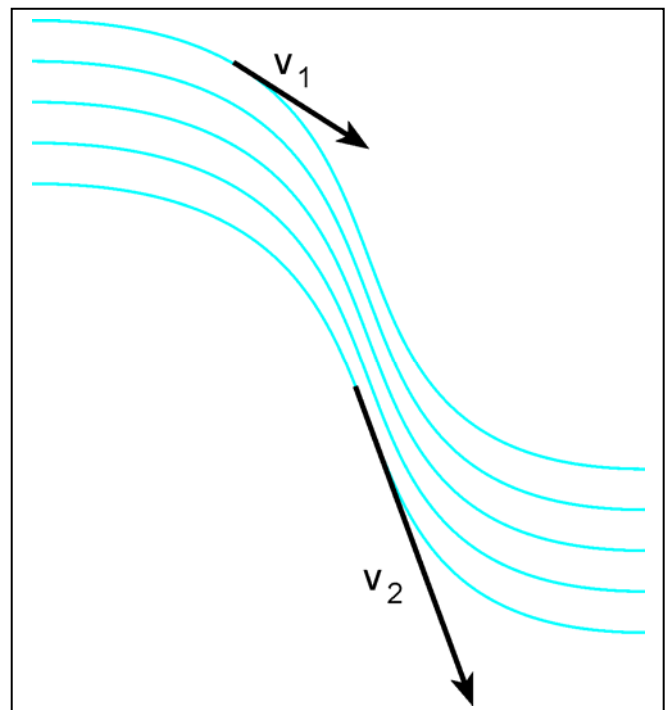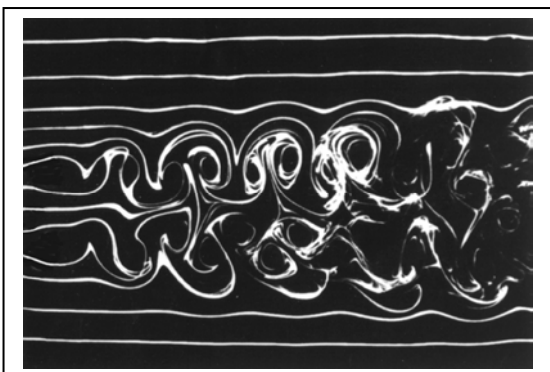**Transport processes**

There are two distinct mechanisms.
The first is when particles of the quantity in question are translocated collectively and this is observable macroscopically, such as in a fluid flow. The other mechanism is where the detected macroscopic translocation is the result of individual motions of particles, which are not observable even microscopically. Diffusion is an example of the latter mechanism.

Flow of fluids and gases (blood-circulation, respiration)

Under ordinary pressure, fluids can be assumed to be incompressible. Gases are naturally compressible, but the pressure differences occuring in the body (for example a few hundred Pascals during breathing) are not normally sufficient to significantly alter gas density. In this sense gases can also be regarded as being essentially incompressible.

For the characterization of fluid flow we can use **streamlines**. At any given point, the tangent of a streamline shows the direction of fluid velocity and the density of streamlines shows the velocity of the flow.

layered flow, or laminar flow and turbulent flow

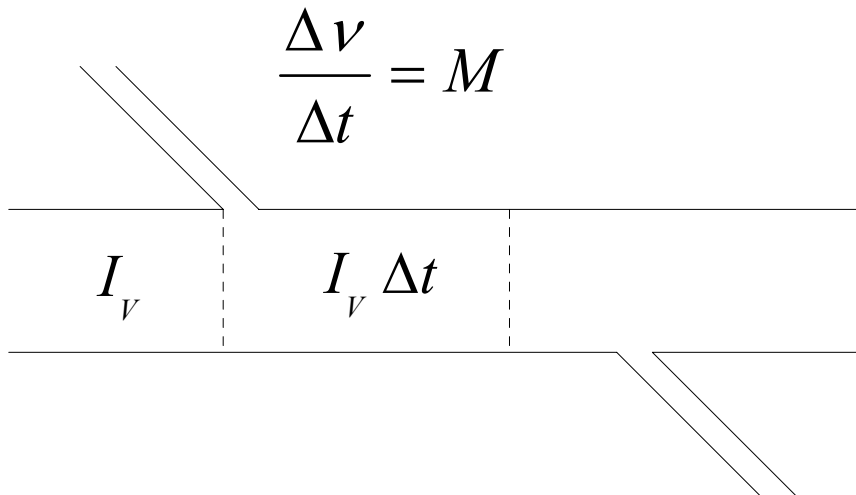Flow can be characterized by the volumetric flow-rate:

$$I_V = \frac{\Delta V}{\Delta t}$$

Methods for measuring the volumetric flow rate:
ultrasound methods (Doppler-examination):

$$f = f_0\left(1 \pm \frac{\upsilon}{c}\right)$$

dilution techniques:

$$\frac{\Delta v}{\Delta t} = M$$

$$I_V \qquad I_V \Delta t$$

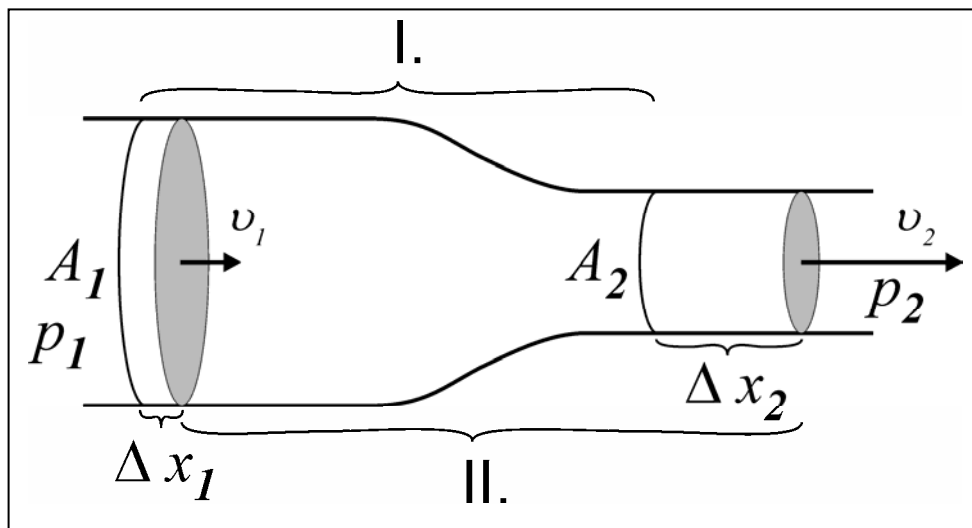$$c = \frac{\Delta v}{I_V \Delta t}$$

Law of continuity

$$I_V = \frac{\Delta V}{\Delta t} = \frac{A \upsilon \Delta t}{\Delta t} = A \upsilon = \text{constant}$$
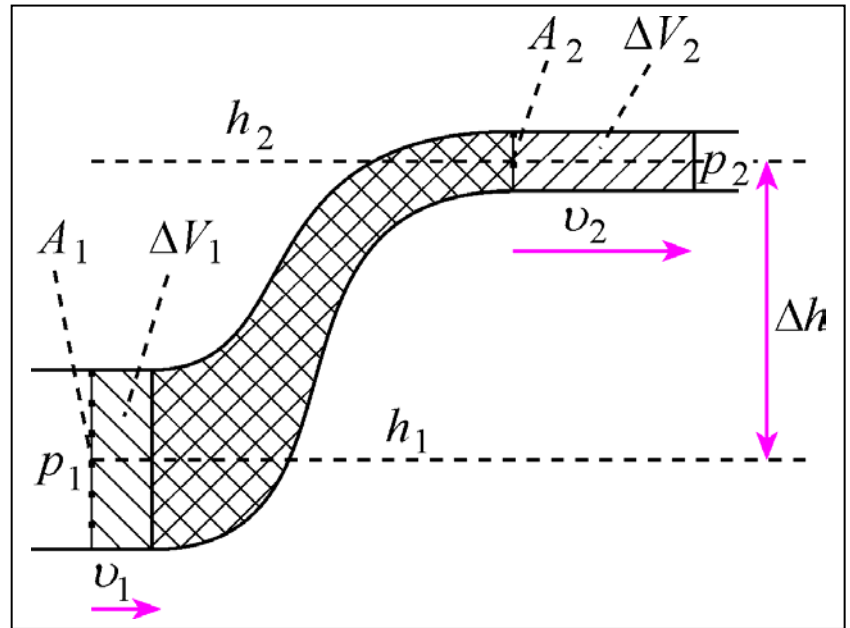
$$I_V = A \overline{\upsilon} = \text{constant}$$

Ideal and real fluids (question of friction)

Bernoulli's law
(for ideal fluids)

Mechanical energy
conservation:
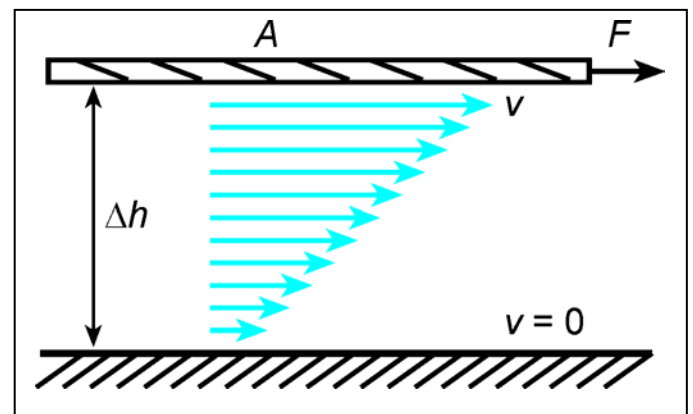
$$W = \Delta E_{kinetic} + \Delta E_{potential}$$

$$p_1 + \frac{1}{2}\rho\upsilon_1^2 + \rho g h_1 = p_2 + \frac{1}{2}\rho\upsilon_2^2 + \rho g h_2 = \text{constant}$$

Consequences

Newton's law of friction

Let fluid flow between two close flat plates and examine what force F has to be exerted to slide the upper plate of surface A with constant velocity υ over the fixed lower plate.

$$F = \eta A \frac{\Delta\upsilon}{\Delta h}$$

η is the coefficient of viscosity or internal friction coefficient (unit: Pa·s)
velocity drop per unit length $\Delta\upsilon/\Delta h$ is constant
Fluids obeying the above equation are called **newtonian fluids**.

3

substance	η (mPa·s) 20 °C
air	(101 kPa) 0.019
water	1
ethanol	1.2
blood (37 °C)	2–8
glycerine	1490
honey	2000–14000

viscosity of gases increases with rising temperature
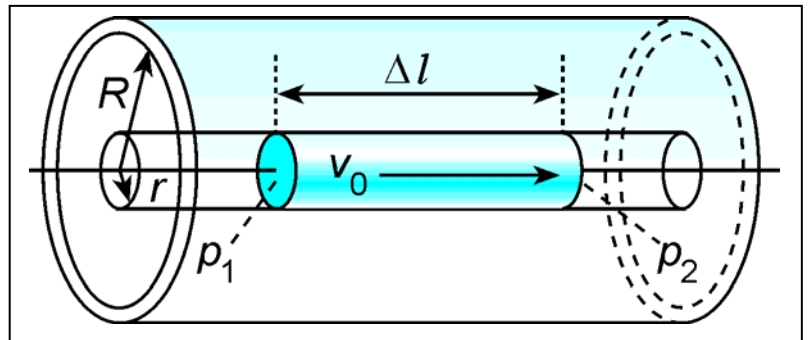
viscosity of fluids decreases with rising temperature

$$\eta \sim e^{\frac{E}{kT}}$$

Fluid flow in a tube

Real fluids show a **linear velocity profile** when flowing between two flat plates very close to each other.

Now, we are going to consider flow in a tube of finite (but not too large) diameter (2R).

Let us consider a tube of fluid of radius r, and length Δl within the original tube, at the ends of which the pressure is p_1 and p_2, ($p_1 > p_2$).

$$F = \Delta p r^2 \pi = \eta 2 r \pi \Delta l \frac{\Delta \upsilon}{\Delta r}$$

from where

$$\frac{\Delta \upsilon}{\Delta r} = \frac{\Delta p}{2 \eta \Delta l} r = -Kr$$

Differential equation:
$$\frac{dv}{dr} = -Kr$$

Solution:
$$v = v_0 - \frac{K}{2}r^2$$

$v = v_0$ at the middle of the tube ($r = 0$) (but $K > 0$) and
$v = 0$ at the borders ($r = \pm R$)

The **velocity profile** ($v(r)$, the flow velocity of the fluid as a function of the radius) is **parabolic.**
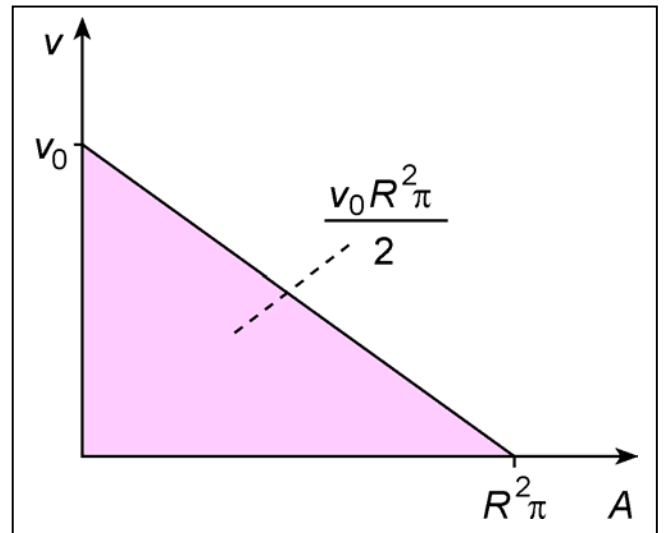
$$v_0 = \frac{1}{2}KR^2$$

Hagen-Poiseuille law and its application to blood-circulation

The most important question is:
what is the volumetric flow rate in the tube?

$$I_V = A\overline{v}$$

$$I_V = \frac{v_0 R^2 \pi}{2} = \frac{1}{4}KR^4 \pi$$

$$I_V = -\frac{1}{8}\frac{\Delta p}{\eta \Delta l}R^4 \pi$$

Hagen-Poiseuille law:
only applies to newtonian fluids undergoing stationary and laminar flow. (The negative sign denotes that fluid flows from the site of higher pressure to the site of lower pressure.)

The volumetric flow rate is directly proportional to the drop of pressure ($\Delta p/\Delta l$) and to the fourth power of the radius.

Blood is a non-newtonian fluid, and **in the arteries** close to the heart, **the flow is not stationary** (away from the heart, stationary flow is a good approximation), **nevertheless the Hagen-Poiseuille law is still a useful approach for investigating blood-circulation**.

Hagen-Poiseuille law's analogy with Ohm's law
(See in the manuel: FLOW)

$$-\Delta p = R_{tube}I_V \quad , \quad U = RI$$

The potential difference corresponds to the pressure difference, the electric current intensity corresponds to volumetric flow rate, and the resistance is analogous to the frictional resistance (tube-resistance) defined by:

$$R_{tube} = 8\pi\eta\frac{\Delta l}{(r^2\pi)^2} \quad , \quad R = \rho\frac{\Delta l}{r^2\pi}$$

Moreover, the resistance of tubes connected in serial and parallel has to be calculated as the resultant resistance of resistors in electronics.

Turbulent Flow

Laminar flow **becomes turbulent if it exceeds a certain critical velocity.** Observations showed that this critical velocity depends on viscosity (η), fluid density (ρ) and the radius of the tube (r):

$$\upsilon_{crit} = \text{Re}\frac{\eta}{\rho r}$$

The coefficient Re is the Reynolds-number, a dimensionless constant (Re $\approx$ 1160 for tubes).

Spherical body moving in a viscous medium

What frictional force acts on a spherical body moving in a fluid?

$$F_s = 6\pi\eta r \upsilon$$

This is Stokes' law. ($F \sim \upsilon$)
The coefficient that relates the two parameters is introduced in the following way:

$$u = \frac{\upsilon}{F} \quad , \quad u = \frac{1}{6\pi\eta r}$$

u is the **mobility** of the sphere, which is the value of the velocity resulting from a unity of force.

Diffusion

Molecular motions can only be observed indirectly.
Brownian motion, is the term used to describe the random motion of the pollens in a suspension, and is the result of continous collisions with otherwise invisible water molecules.

Characteristics of molecular motion

The description of molecular motion is much more complicated in fluid phase than in gases, thus we present the basic diffusion laws for gases, but the results are applicable under certain conditions to fluids too.

Earlier we learned the average kinetic energy of a single particle in thermal equilibrium (model of the ideal gas):

$$\bar{\varepsilon}_{kin} = \frac{1}{2} m \overline{\upsilon^2} = \frac{3}{2} kT.$$

The **average time between collisions** is denoted by τ, and the average distance travelled between two collisions, or the so-called **mean free path** is denoted by l. Thus

$$l = \upsilon \tau.$$

When an **external field** is appiled, some of the particles' path is still zig-zagged, but a unidirectional drift is added to the random motion. (For example a portion of gas-particles are ionized and the applied external field is electric.)
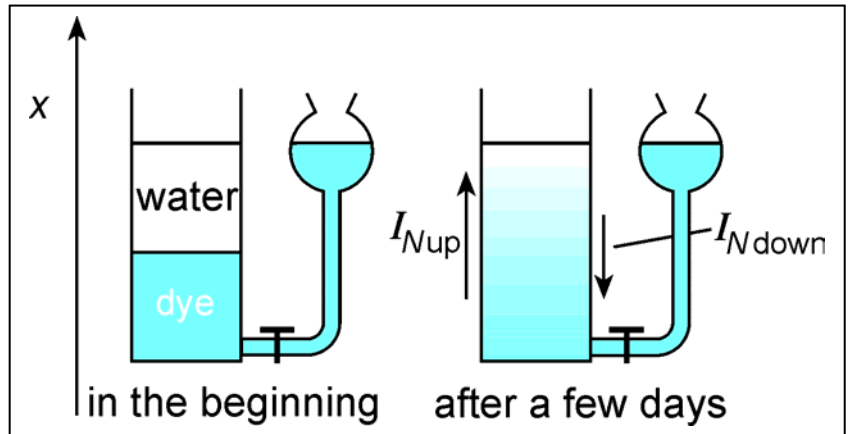Using Newton's second law the **drift speed**

$$\upsilon_{drift} = \frac{F}{m} \tau,$$

and the **mobility**

$$u = \frac{\upsilon_{drift}}{F} = \frac{\tau}{m}.$$

Diffusion phenomena, Fick's first law

Spreading of particles because of the random thermal motion called **diffusion.** It continues until the distribution of the particles is uniform throughout the entire volume.

Diffusion takes place in two-component systems most of the time: for example let A denote **the diffusing component**, and B **the medium, in which it diffuses**. "A" can be the dye, and "B" is the water.

The **particle-flux** is:

$$I_N = \frac{\Delta N}{\Delta t},$$

where ΔN is rhe number of particles travelling through a certain surface A in a time-interval Δt. For experimental use, it is more convenient to use the **matter flow rate.** (In this case, the amount of substance is expressed in moles.)
Since $\Delta v = \Delta N / N_A$, where N_A is the Avogadro's number, the matter flow rate (I_v) through the surface A is:
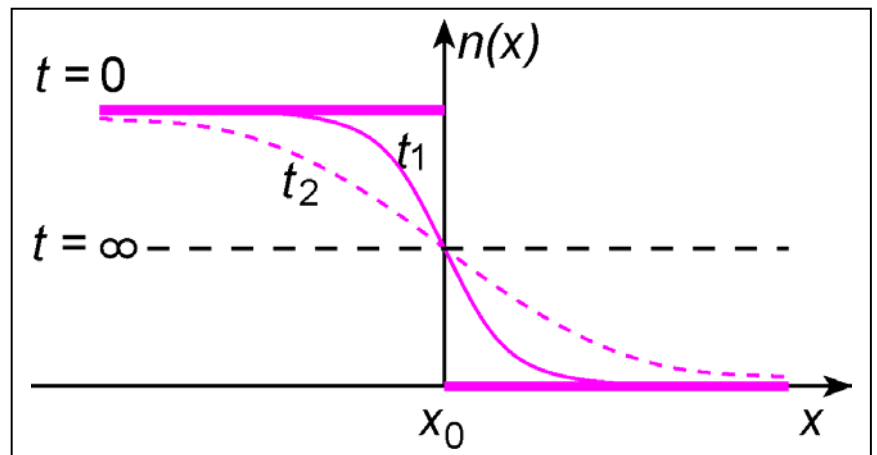
$$I_v = \frac{\Delta v}{\Delta t}.$$

The unit of the matter flow rate is mol/s. For the following calculations, it is practical to introduce the **matter flow density**:

$$J_v = \frac{\Delta I_v}{\Delta A}.$$

Fick interpreted diffusion along the concept of Brownian motion, which was known by that time.

Each dye molecule undergoes random thermal motion, and the molecules can travel in any direction with equal probability. In this situation, if x denotes the direction parallel to the longitudinal axis of the container, then two particle fluxes form, one upwards (denoted by I_{Nup}) and another one downwards (denoted by I_{Ndown}). Since the number of dye molecules is higher at the bottom of the container than in the upper regions in the beginning of the process, $I_{Nup} > I_{Ndown}$, thus the net particle-flux (or net substance transport) proceeds upwards, its value equals $I_{Nup} - I_{Ndown}$.

What does the diffusion rate depend on and what will be the size of the flux-density (J_v) of the blue particles?

$$J_v = -D \frac{\Delta c}{\Delta x}$$

This is **Fick's first law**. The meaning of $\Delta c / \Delta x$ is the concentration drop of a unit-length, or concentration-gradient.
The most important message of the law is that the matter flow which characterizes the "strength" of diffusion is proportional to the drop in concentration. The proportionality coefficient is the called **diffusion coefficient.**

$$D = ukT$$

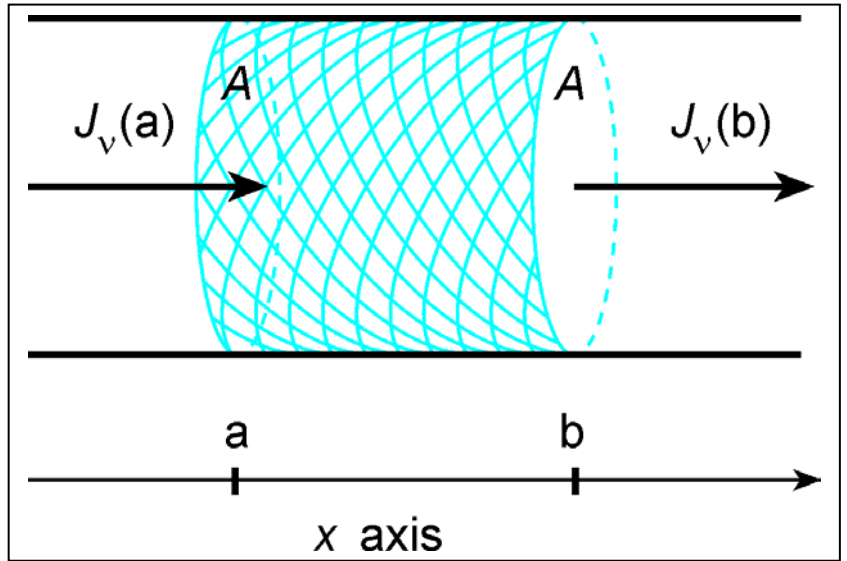its dimension is: m^2/s.

$$D = \frac{kT}{6\pi\eta r}$$

This is the **Stokes-Einstein equation.**

Fick's second law
(describes the concentration's spatial and temporal variation)

The equation can be derived quite simply from Fick's first law, if we generalize the equation of continuity.

$$J_v(a)A - J_v(b)A = 0$$

Which expresses the fact: the amount of substance that fluxed in through a surface of A equals the amount of substance effluxed.

If there is a net substance influx into the space enclosed by a and b, then this amount of substance has to appear in the given volume. Thus the concentration of the substance (c) will grow there during net influx.

Let a = x and b = $x + \Delta x$ be very close to each other.

$$\left[J_v(x)A - J_v(x + \Delta x)A\right]\Delta t = \left[c(t + \Delta t) - c(t)\right]A\Delta x$$

$$-\frac{\Delta J_v}{\Delta x} = \frac{\Delta c}{\Delta t} \qquad \left(J_v = -D\frac{\Delta c}{\Delta x}\right)$$

This is the **generalized continuity-equation**. Let's replace (J_v) from Fick's first law:

$$D\frac{\Delta\left(\dfrac{\Delta c}{\Delta x}\right)}{\Delta x} = \frac{\Delta c}{\Delta t}, \qquad \left(D\frac{\partial^2 c}{\partial x^2} = \frac{\partial c}{\partial t}\right)$$

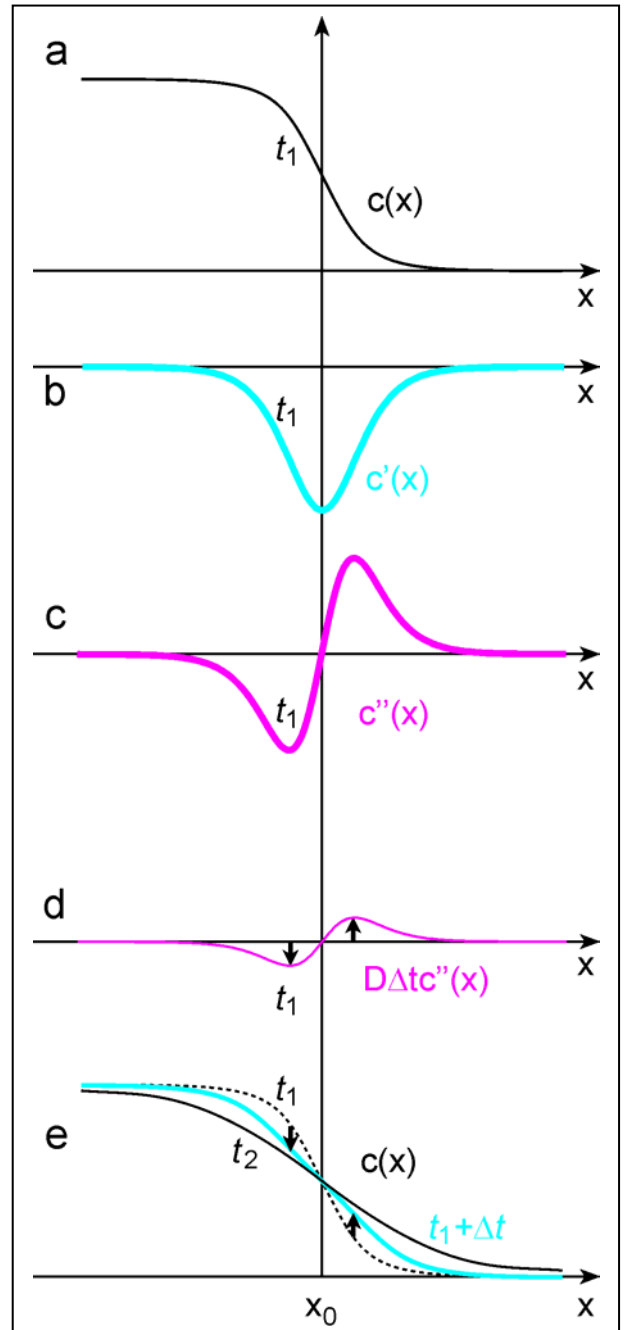This is **Fick's second law.** (See in the manuel: DIFFUSION)

Meaning of Fick's second law

With the aid of numeric methods, and the knowledge of all initial conditions, the concentration's temporal and spatial alteration can be determined with good accuracy.

$$D\frac{\Delta\left(\dfrac{\Delta c}{\Delta x}\right)}{\Delta x}\Delta t + c(t) = c(t+\Delta t)$$

This expression give us the concentration a little later $(t + \Delta t)$ time-point,
if its (spatial) distribution at a time point (t) was known.
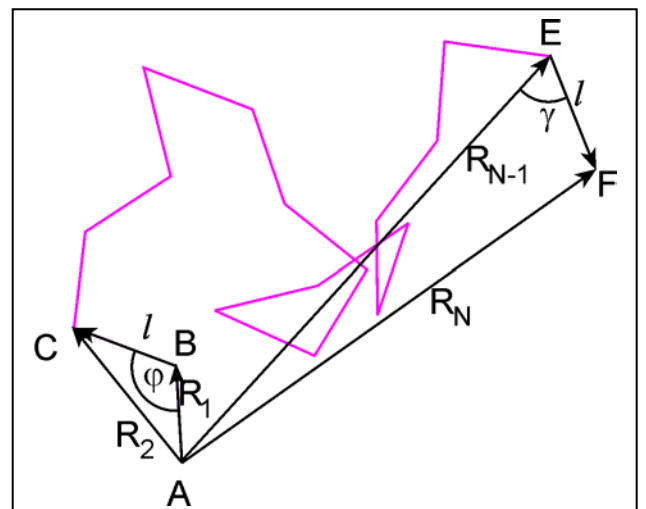
$$c(t) + c''D\Delta t = c(t+\Delta t)$$

Random-walk problem
How far does the particle get from its initial position, because of the thermal motion?

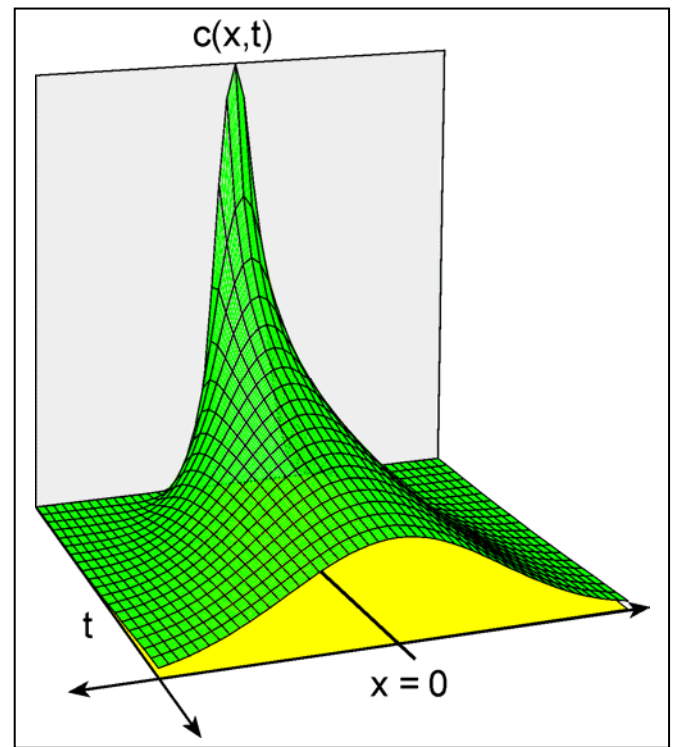$$R_2^2 = l^2 + l^2 - 2l^2\cos\varphi$$

$$\overline{R_N^2} = \overline{R_{N-1}^2} + l^2 = Nl^2$$

$$\overline{R(t)} = \sqrt{3Dt}$$

$$\sigma_x \sim \overline{R(t)} \sim \sqrt{Dt}$$

(The random-walk problem is sometimes called the problem of the "drunk sailor". The sailor comes out from the pub and sets off somewhere, but since his legs do not always obey his will, his steps are random. Every step is randomly angled to that of the previous one. Given these circumstances how far does the sailor get after a set amount of time? Naturally, we do know exactly, because it is not determinable, but we can calculate the average distance the sailor takes if the incident is repeated daily.)
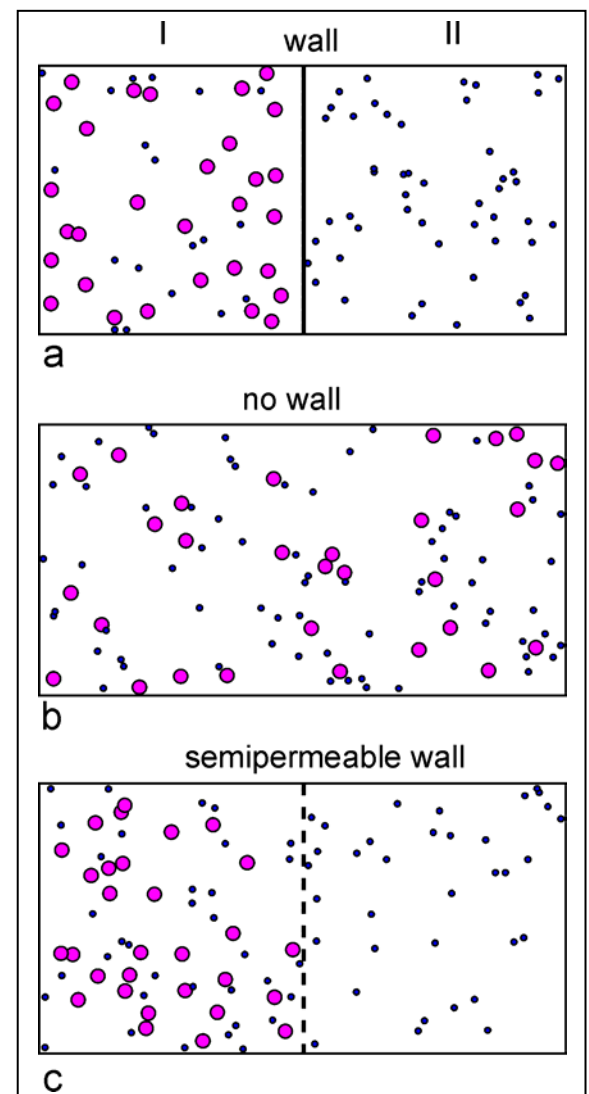
Osmotic phenomenon

A small-sized, semi-permeable bag, filled with sugar dissolved in water is placed in a container filled with pure water. After a certain time, we can observe the bag swelling, and that ouside of it in the container the water remains pure, while the solution in the bag has been diluted.

This **unidirectional matter flow, which takes place by means of diffusion, is called osmosis**.

van t'Hoff law: $p_{osmotic} = cRT$.

If osmotic pressure is equal in two different solutions, we call them isotonic solutions.

Thermodynamic aspects of transport processes

Thermodiffusion:

one end of a U-shaped pipe with Na_2SO_4-salt solution was heated with hot steam, and the other end was cooled with ice. Due to the temperature difference, dissolved salt migrated from the warmer section of the pipe to the colder section. (Ludwig–Soret-effect)
The law that describes this phenomenon is:

$$J_v = -L_T \frac{\Delta T}{\Delta x} .$$

We can see that this equation is very similar to Fick's first law, so the coefficient L_T corresponds in some sense to the diffusion coefficient.

Heat conduction

If the net particle flux is zero, means the same number of particles cross the wall from left to right as right to left, but the temperature-difference between the two sides is maintained, we are faced with another phenomenon (Fourier).

$$J_E = -\lambda \frac{\Delta T}{\Delta x} .$$

Thermodynamic system

This can be a gas of a given volume, a bacterium, a lymphocyte, an animal or a human, but it can also be a part of the body, like the heart, or even the Earth as a whole.
Any other substance in interaction with the examined system is called the **environment**.

type	matter exchange	energy-exchange
isolated	–	–
closed	–	+
open	+	+

Extensive and intensive quantities

Quantities that behave like volume when dividing the system into sub-systems ($V_{total} = V_1 + V_2$) are called **extensive** quantities.
Energy (E), mass (m), charge (Q), and number of particles (N) are all like this. (They are proportional to the "size" of the system.)

We call our system **homogenous**, if any division of the system, by any of the extensive quantities can be written up as

$$\frac{x_{total}}{V_{total}} = \frac{x_{subsystem}}{V_{subsystem}} .$$

In homogenous thermodynamic systems there are quantities, which value remains the same after division into sub-systems. These are **intensive** quantities.
Pressure (p) and temperature (T) are all like this. (They are independent of the "size" of the system.)

Uniform description of transport processes

Every transport process is caused by an inhomogeneity. The inhomogeneity can be determined by measuring the **differences in intensive quantities**. Transport takes place to decrease these differences between sub-systems. It can only be achieved by a **flux of some extensive quantities**.

The formal similarity among the laws of transport processes, reveal a more general rule, known as the **Onsager-relation**:

$$J = LX , \text{ where}$$

$J = \dfrac{\Delta x_{extensive}}{A\Delta t}$ **flux-density** of the flowing extensive quantity

$X = \dfrac{-\Delta y_{intensive}}{\Delta x}$ **thermodynamic force** exerted by the gradient of the corresponding intensive quantity

L is the so-called **conductivity coefficient**. (if $X = 0$, **equilibrium**)

Laws of thermodynamics

A condition for equilibrium was that intensive quantities associated with the different interactions are uniform throughout the system. This is the **zeroth law of thermodynamics**.

First law of thermodynamics (energy-conservation)
The change in the internal energy (ΔE) of the system is equal to the sum of the transfer of heat (Q_E) to the system and the work being done on the system (W):

$$\Delta E = Q_E + W$$

The **internal energy** consists of the kinetic and interactional (structural) energy and it does not include the kinetic and potential energies of the macroscopic system as a whole.

Originally, we only took account of mechanical interaction when calculating the work being done on the system, thus it has a very simple form:

$$W = -p\Delta V \, .$$

The work done by other forces (electric, material etc.):

$$W_Q = \varphi\Delta Q \, , \; W_\nu = \mu\Delta\nu \, ,$$

where φ and Q note the electric potential and the charge, μ is the chemical potential, ν is the number of moles.

Since the ionic charge of ν moles of ions of z valency is $Q = zF\nu$ (F is the Faraday-constant, $F = N_A q_e$), the work terms of the two interactions can be fused:

$$W_{\nu Q} = \mu\Delta\nu + \varphi\Delta(zF\nu) = (\mu + zF\varphi)\Delta\nu = \mu_e\Delta\nu$$

where μ_e the so-called **electro-chemical potential**.

(In the discussion of transport processes across membranes, we will encounter this quantity many times, as the intensive quantity of ionic fluxes.)

Second law of thermodynamics

Only those processes proceed in isolated systems where intensive quantities that characterize interactions are to be equilibrated.

The characteristic extensive quantity associated with thermal interaction is called as **entropy** and denoted by S.

$$Q_E = T\Delta S$$

Let's investigate the change of entropy in a spontaneous thermalization process.

E_1 and E_2 are the internal energies of the subsystems $(T_1 \neq T_2)$.

The first law of thermodynamics for the subsystems, which consists of only one term in this case:

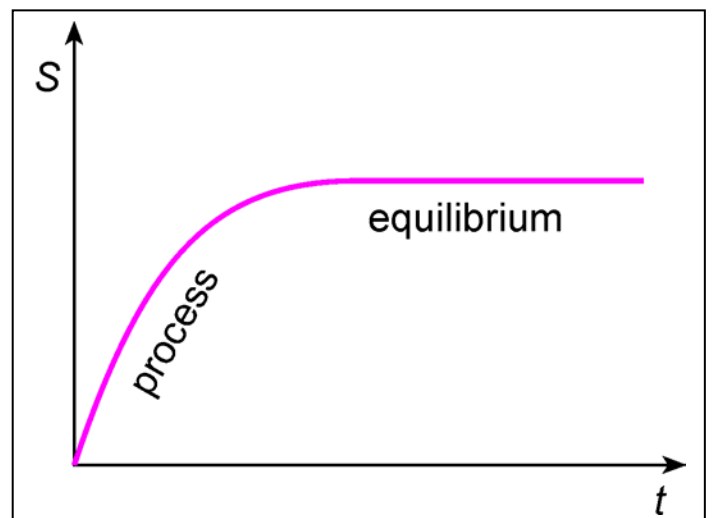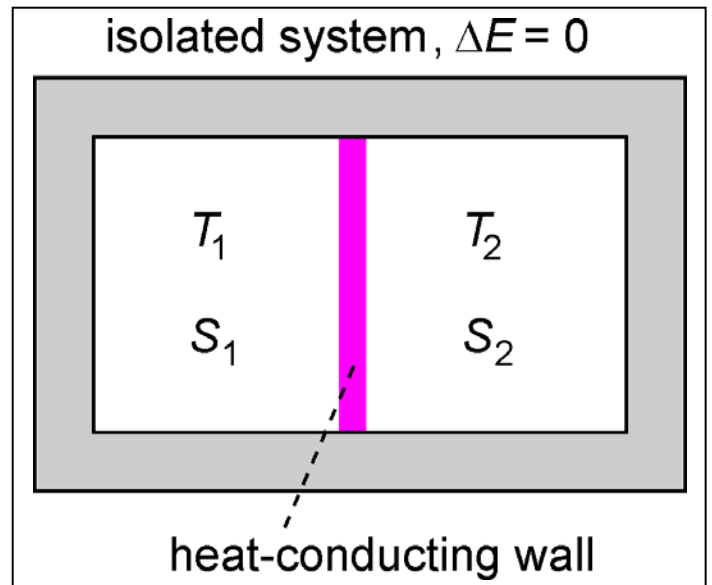$$\Delta E_1 = T_1 \Delta S_1, \quad \Delta E_2 = T_2 \Delta S_2.$$

Regarding the fact, that entropy is an extensive quantity and $\Delta E_1 = -\Delta E_2$:

isolated system, $\Delta E = 0$

T_1 T_2

S_1 S_2

heat-conducting wall

$$\Delta S = \Delta S_1 + \Delta S_2 = \frac{\Delta E_1}{T_1} + \frac{\Delta E_2}{T_2} = \Delta E_1 \left(\frac{1}{T_1} - \frac{1}{T_2} \right).$$

If $T_1 > T_2$ initially, then the first subsystem cools in the process, thus its internal energy is decreased, i.e. $\Delta E_1 < 0$, but in this case $(1/T_1 - 1/T_2) < 0$.

Oppositely...Consequently, **the entropy of an isolated system always increases during the process of thermalization**. Entropy does not conserve.

S

process

equilibrium

t

Statistical definition of entropy

Microstate: microscopic parameters (for example position and velocity) of all the elements of the system are known.

Macrostate: distribution of macroscopic parameters (for example temperature, pressure, density etc.).

One macrostate can be realized by a lot of microstates.
The number of microstates that belong to the same macrostate is called **thermodynamic probability**, and its sign is Ω. (Most probable macrostate, $\Omega_{AB} = \Omega_A \Omega_B$, $S_A + S_B = S_{AB}$)

$$S = k \ln \Omega$$

where k is the Boltzmann constant (less probable and more probable states). Entropy, by its nature, never decreases spontaneously.

Third law of thermodynamics
The entropy of a single-component, crystallizing material is 0 at 0 K temperature.

$$S = k \ln 1 = 0$$

Thermodynamic potential functions
Note: (for small changes)
$$\Delta(pV) = (p + \Delta p)(V + \Delta V) - pV$$
$$pV + p\Delta V + V\Delta p + \Delta p \Delta V - pV \approx p\Delta V + V\Delta p$$
If p = const. $\Delta p = 0$ and
$$\Delta(pV) \approx p\Delta V$$

$$\Delta E = Q_E - p\Delta V \Rightarrow \Delta(E + pV) = Q_E = \Delta H$$

Change of enthalpy: ΔH
Thus, the fact that enthalpy is a state function is identical with **Hess' law**, which had been formulated much earlier.

Closed system
(isolated as a whole)

$$\Delta S_{\text{total}} = \Delta S_{\text{s}} + \Delta S > 0$$

$$\Delta S = -\frac{Q_E}{T}$$
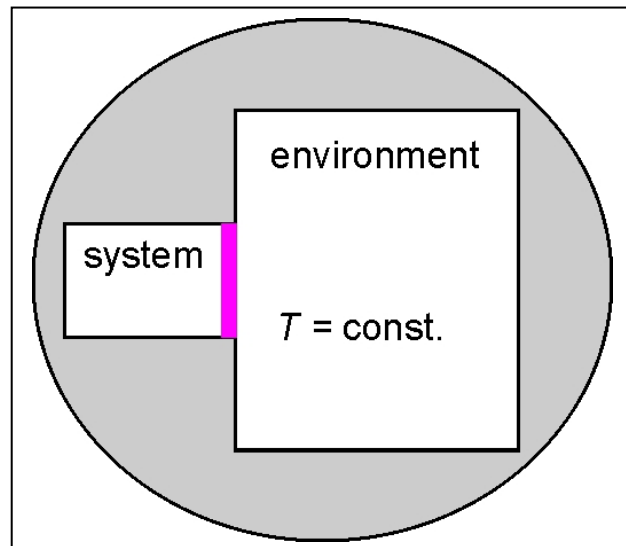
$$T\Delta S_s > Q_E = \Delta E$$

Since T = const. $\Delta T = 0$ thus

$$\Delta(TS) \approx T\Delta S$$

$$0 > \Delta E - T\Delta S_s = \Delta(E - TS) \equiv \Delta F < 0$$

Change of Helmholtz free-energy: $\Delta \boldsymbol{F}$

Closed system with "moving" wall
(isolated as a whole)

$$\Delta S_{\text{total}} = \Delta S_{\text{s}} + \Delta S > 0$$

$$\Delta S = -\frac{Q_E}{T}$$

$$T\Delta S_s > Q_E = \Delta E + p\Delta V$$

Since $\Delta T = 0$ and $\Delta p = 0$ thus

$$\Delta(TS) \approx T\Delta S \; ; \Delta(pV) \approx p\Delta V$$

$$0 > \Delta E - T\Delta S_s + p\Delta V = \Delta(E - TS + pV) \equiv \Delta G < 0$$

Change of Gibbs free-energy (free enthalpy): $\Delta \boldsymbol{G}$