Chapter 20
Transport Phenomena

Diffusion can play an important role for the kinetics of chemical reactions in solutions. We use that as an opportunity to discuss this process of molecular motion more closely. The migration velocity is determined by a gradient of chemical potential and therefore eventually by a concentration gradient. This leads us to the quantitative description with the help of Fick's law of diffusion. But not only matter can be transported from one place to another but also some other properties such as entropy or momentum. *Entropy conduction* is determined by the migration of entropy down a temperature gradient and *viscosity* by a migration of linear momentum down a velocity gradient. In order to carve out the commonalities and differences of the transport phenomena discussed, they are summed up in the last section and compared with the transport of electric charge, because the latter is the best known of these phenomena.

20.1 Diffusion-Controlled Reactions

In order for bimolecular or trimolecular reactions to even occur, the reacting particles must collide with each other. As we have learned, not every collision leads to a reaction. The particles involved must bring the necessary energy for forming the generally energy-rich transition complex, and not all of them do. The microscopic velocity of the particles is basically the same in all states of aggregation at the same temperature. However, compared to gases, their mobility in liquids, and especially in solids, is very low. In the extreme case of crystals, their motion is limited to a fast oscillation around a position of rest. Only occasionally does a switching to an interstitial site or a change of position occur. As the particles transition from gas to solid, i.e., with increasing condensation, the frequency of collisions and the average residence time of one particle in the neighborhood of another rise. Gas particles colliding with each other is a very fleeting occurrence, after which the partners immediately separate. In liquids, though, the particles

G. Job, R. Rüffler, *Physical Chemistry from a Different Angle*,
DOI 10.1007/978-3-319-15666-8_20

colliding with each other are crowded by their neighbors and often remain together for a good while.

If the activation threshold $\Delta_{\ddagger}\overset{\circ}{\mu}$ vanishes or is very low, just about every encounter will lead to a reaction. Hence, it is not the height of this potential threshold but the frequency of collisions that then determines the conversion rate. In this case, the concentration of the transition complex can remain far below its equilibrium value because continued supply is stalled, while decomposition continues taking place. Reactions of this kind are said to be *diffusion-controlled* (or *diffusion-limited*) because their collision frequency is dependent upon the diffusion rate (diffusion velocity) of the partners involved. Bimolecular reactions in water and similarly viscous liquids are of this type if the activation threshold sinks under the third or fourth rung of our "potential ladder," meaning that $\Delta_{\ddagger}\overset{\circ}{\mu} < 20\ \mathrm{kG}$ (see Fig. 18.2). Because diffusion in solid substances proceeds incomparably slowly, almost all the bimolecular reactions in such an environment are diffusion-controlled.

We will take this opportunity to discuss the transport of substances by diffusion and the transport phenomena associated with it. Entropy transport is often closely coupled with transport of substances so we will include it as well.

20.2 Rate of Spreading of Substances

Mobility All dissolved substances migrate under the influence of external forces. Gravitational influences will cause them to sink; they will follow the centrifugal force in a centrifuge or diffuse due to "chemical forces." (In Sect. 12.2, we were introduced to the term *diffusion* as spreading of substances caused by a potential gradient and therefore essentially by differences of concentration.) There is a unified approach that can describe all these processes. Measurements show that the migration velocity of a substance B, or the particles it is made up of, does not depend upon types of forces (be they mechanical, chemical, or electrical) but only upon their magnitude. If the forces are not too great, we can assume the migration velocity v_{B} to be proportional to the effective force F_{B}:

$$v_{\mathrm{B}} = \omega_{\mathrm{B}} \cdot \frac{F_{\mathrm{B}}}{n_{\mathrm{B}}}. \tag{20.1}$$

n_{B} is the amount of substance B. The fact that v_{B} is proportional to the quotient $F_{\mathrm{B}}/n_{\mathrm{B}}$ and not to F_{B} makes sense because if the amount of migrating substance is doubled, the force upon a given portion of the substance will be halved. The migration velocity then behaves no differently than the velocity of a train of tugged barges with the number n of barges (Fig. 20.1). We call the factor ω_{B} the mechanical *mobility* of substance B. The quantity has the unit $\left(\mathrm{m\,s^{-1}}\right)/\left(\mathrm{N\,mol^{-1}}\right) = \left(\mathrm{m\,s^{-1}}\right)/\left(\mathrm{kg\,m\,s^{-2}\,mol^{-1}}\right) = \mathrm{s\,mol\,kg^{-1}}$.

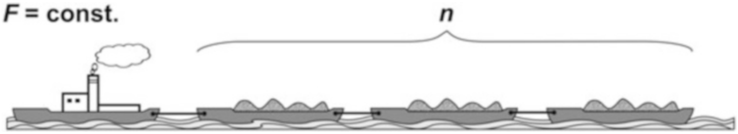
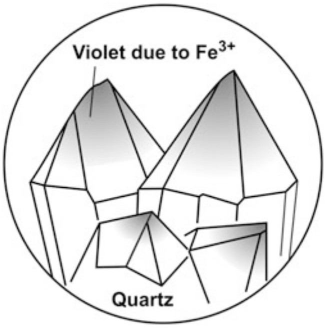
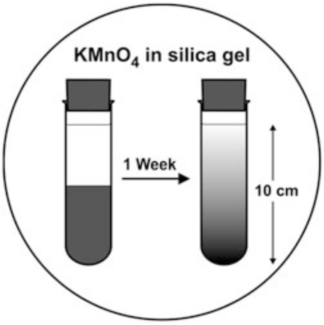


Fig. 20.1 Velocity v of a train of barges with n tugged barges to demonstrate the concept of migration velocity v of a substance if the amount n to be moved is increased while force F is kept constant.

Experiment 20.1 *Unevenly colored crystals as an example of an extremely small diffusion velocity*: Even after millions of years, amethysts, a violet variety of quartz, can exhibit uneven violet coloring due to diffusing Fe^{3+} ions. In spite of its great age, an even distribution has not been achieved. The color itself results from Fe^{4+} ions which are formed by irradiation of Fe^{3+} ions (e.g., with naturally occurring isotopes).



Experiment 20.2 *Diffusion of permanganate in silica gel*: Sodium silicate is acidulated, whereby clear silica gel is produced. One half of the gel is colored by permanganate and poured into a large test tube. The colorless half is then also poured into the test tube. After a week, the MnO_4^- ions have already covered a distance of a few centimeters. The process can be followed easily using the violet color as indicator.



Mobility of particles in crystals [like for example quartz (SiO_2)] at room temperature is extremely low (Experiment 20.1).

The electrons in metals are an exception. In good conductors, they are around ten times as mobile as gas molecules in air.

But let us now have a look at the spreading of particles in liquids or gels. In silica gel, which is mostly made up of water, violet-colored MnO_4^- ions require about one week to move a distance of a few centimeters (Experiment 20.2). We use gel instead of a liquid to avoid convective disturbances in diffusion.

We find similar values of diffusion velocities and relatively unified conditions in liquids. Table 20.1 shows mobilities for various types of particles in water. The values are valid for very small concentrations, meaning practically pure water,

Table 20.1 Mobility of various kinds of particles in water. The values are valid for 298 K and for very small concentrations.

Substance	Ar	CO_2	D_2O	Na^+	Cl^-
ω_0 (10^{-12} s mol kg^{-1})	0.91	0.73	1.00	0.538	0.820

ω values in other environments are presented for comparison (Table 20.2)

Table 20.2 Mobility of various kinds of particles in differing environments at a temperature of 298 K.

Substance	e^- (in silver)	Cu (in silver)	Na^+ (in table salt)	CO_2 (in air)
ω_0 (s mol kg^{-1})	6×10^{-8}	10^{-41}	10^{-35}	6×10^{-9}

which is indicated by the index $_0$. (We use the slashed zero for clarity.) ω values in other environments are presented below for comparison (Table 20.2).

Despite the low viscosity of water, the mobility of particles in aqueous solutions is surprisingly low. The weight (force of gravity) in the Earth's gravitational field, for example, is much too small to evoke any noticeable effect. Only the enormous forces in ultracentrifuges can cause an observable spreading of substances. If all other influences could be ignored, carbon dioxide in water in the Earth's gravitational field would sink at the extremely small velocity of about 1 mm per century. Because $F_B = m_B g = n_B M_B g$, we have:

$$\begin{aligned} v_B &= \omega_B M_B g \\ &= 0.73 \times 10^{-12}\,\mathrm{s\,mol\,kg^{-1}} \times 0.044\,\mathrm{kg\,mol^{-1}} \times 9.81\,\mathrm{m\,s^{-2}} \\ &= 0.32 \times 10^{-12}\,\mathrm{m\,s^{-1}} \approx 10\,\mu\mathrm{m\,a^{-1}}. \end{aligned}$$

In contrast, particles in gases have a high mobility. We showed this in Experiment 12.3 (spreading of Br_2 in air).

Diffusion In Chap. 12, we were introduced to the driving force behind the spreading of substances that we call diffusion. This is the diffusion force F_B, which is dependent upon the gradient of the chemical potential:

$$F_B = -n_B \cdot \frac{d\mu_B}{dx}.$$

If substance B is mobile, it will migrate in the direction of the potential gradient at a velocity which results from combining Eqs. (12.1) and (20.1):

$$v_B = -\omega_B \cdot \frac{d\mu_B}{dx}. \qquad (20.2)$$

A flow of matter is generated in the direction of a drop in chemical potential. v_B is a (virtual) drift velocity, which results from the much faster, mostly erratic and random, actual (Brownian) molecular motion. In order to achieve a handier description of this process, we will introduce the following established quantities.

The *throughput* (of matter) is the amount of substance Δn_B passing through a given cross-sectional area A in the time span Δt (Fig. 20.2). This includes all the particles that are not farther away than $\Delta x = \upsilon_\mathrm{B} \cdot \Delta t$ from area A, i.e., all the particles inside the (dashed) cuboid with the volume $A \cdot \Delta x = A \cdot \upsilon_\mathrm{B} \cdot \Delta t$. We find the amount of substance when we multiply this volume by the substance concentration c_B:

$$\textit{Throughput}\colon \Delta n_\mathrm{B} = c_\mathrm{B} \cdot A \cdot \upsilon_\mathrm{B} \cdot \Delta t. \tag{20.3}$$

We can derive other useful quantities from the throughput such as *matter flux* (or *current of amount of substance*) J_B as well as *flux density* (or *current density*) (of matter) j_B, which denotes the flux per area through which the flow passes:

$$\textit{Matter flux}\colon J_\mathrm{B} = \frac{\Delta n_\mathrm{B}}{\Delta t} = c_\mathrm{B} \cdot A \cdot \upsilon_\mathrm{B}, \tag{20.4}$$

$$\textit{Flux density}\ \text{(of matter)}\colon j_\mathrm{B} = \frac{J_\mathrm{B}}{A} \quad \text{or} \quad j_\mathrm{B} = c_\mathrm{B} \cdot \upsilon_\mathrm{B}. \tag{20.5}$$

The relation with the chemical potential gained from Eq. (20.2) can be used for υ_B, where $c_\mathrm{B} \cdot \omega_\mathrm{B}$ appears as a kind of conductivity σ_B for substance B:

$$j_\mathrm{B} = -c_\mathrm{B} \cdot \omega_\mathrm{B} \frac{\mathrm{d}\mu_\mathrm{B}}{\mathrm{d}x} \quad \text{with “matter conductivity”} \quad \sigma_\mathrm{B} = c_\mathrm{B} \cdot \omega_\mathrm{B}. \tag{20.6}$$

Law of Diffusion The flow of matter in a homogeneous environment at low concentration c_B represents an important special case. Here, the concentration, and indirectly the position dependency of the chemical potential, can be expressed by the mass action equation:

$$\mu_\mathrm{B}(x) = \mu_{\mathrm{B},0} + RT \ln \frac{c_\mathrm{B}(x)}{c_{\mathrm{B},0}}. \tag{20.7}$$

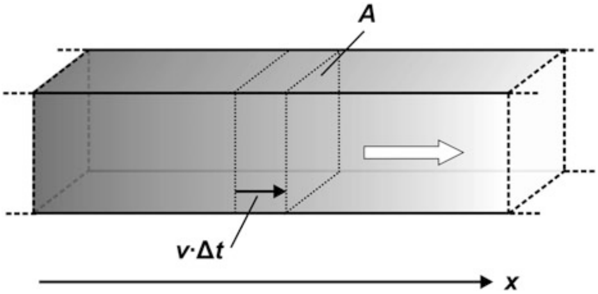


Fig. 20.2 Schema of the relationship of migration velocity υ, concentration c, and matter flux J or flux density j.

In order to obtain an expression for the potential gradient $\mathrm{d}\mu_B(x)/\mathrm{d}x$, we must take the derivative with respect to x at constant T. Taking the chain rule into account, we obtain (compare Sect. A.1.2 in the Appendix):

$$\frac{\mathrm{d}\mu_B(x)}{\mathrm{d}x} = \frac{RT}{c_B(x)} \cdot \frac{\mathrm{d}c_B(x)}{\mathrm{d}x}. \tag{20.8}$$

A few words about the calculation. The term $\mu_{B,0}$, which is constant, drops out when taking the derivative. The constant factor RT remains. The derivative of the logarithmic function $y = \ln x$ yields the reciprocal of its argument, meaning $1/x$, whereby a constant factor there (in this case, the factor $1/c_{B,0}$) can be omitted. The reason for this omission is simply that $\ln(ax) = \ln a + \ln x$, and in taking the derivative, the constant expression $\ln a$ disappears. The intermediate result is $RT/c_B(x)$. According to the chain rule, we must still multiply this result by the derivative of the "inner" function $c_B(x)$. This means multiplying by $\mathrm{d}c_B(x)/\mathrm{d}x$, as in Eq. (20.8) above.

With the help of this equation, we obtain the following expression for the drift velocity v_B and the flux density j_B:

$$v_B = -\omega_B \cdot \frac{\mathrm{d}\mu_B}{\mathrm{d}x} = -\omega_B \cdot \frac{RT}{c_B}\frac{\mathrm{d}c_B}{\mathrm{d}x} \quad \text{or} \quad j_B = c_B \cdot v_B = -\omega_B RT \frac{\mathrm{d}c_B}{\mathrm{d}x}. \tag{20.9}$$

The flux density is proportional to the concentration gradient. The expression ωRT is usually abbreviated to D and called the *diffusion coefficient* (unit $\mathrm{m}^2\ \mathrm{s}^{-1}$). This relation was first set up in this form by the German physiologist Adolf Eugen Fick in the year 1855:

$$j_B = -D_B \cdot \frac{\mathrm{d}c_B}{\mathrm{d}x} \quad \text{Fick's (first) law of diffusion.} \tag{20.10}$$

The relation between ω_B (or a corresponding quantity) and D_B was only discovered in 1908, almost simultaneously by Albert Einstein and Marian von Smoluchowski:

$$D_B = \omega_B RT \quad \text{Einstein-Smoluchowski equation.} \tag{20.11}$$

Table 20.3 shows some values for diffusion coefficients in water.

Table 20.3 Diffusion coefficients of some substances in water at 298 K (catalase at 293 K) in the limit of vanishing concentration. The value for water can be determined experimentally by using H_2O molecules marked with isotopes (such as $H_2{}^{17}O$).

Substance	D_0 ($10^{-9}\ \mathrm{m}^2\ \mathrm{s}^{-1}$)
Water	2.26
Hydrogen	5.11
Carbon dioxide	1.91
Acetate ion	1.29
Glucose	0.67
Catalase	0.041

While D_B in liquids at room temperature and standard pressure is of the order of 10^{-9} m^2 s^{-1}, the value for gases lies much higher, at around 10^{-4} m^2 s^{-1}. It is, however, many orders of magnitude lower for solid substances.

The diffusion coefficient depends upon the temperature, not so much because of the factor T appearing in Eq. (20.11), but because ω_B itself is not constant. In liquids and especially in solids, moving particles have considerable attractive forces to overcome—meaning, there will be an activation threshold. If we assume a temperature dependency with a molar activation energy W_A corresponding to the Arrhenius equation, we obtain

$$D_B \sim e^{-W_A/RT}. \qquad (20.12)$$

This strong temperature dependency, which is caused by the exponential expression that is "hidden" behind ω_B in the equation above, masks all the other influences such as the linear dependency of T. For this reason, a diffusion coefficient of a magnitude of 10^{-24} m^2 s^{-1} in a solid substance at low temperatures can climb to 10^{-8} m^2 s^{-1} at temperatures of 1,500 K.

Duration of Concentration Equalization In order to get an impression of how fast a uniform distribution of substances at room temperature in a limited space can happen, we will consider a container in which an artificial linear concentration gradient along its largest diameter l has been created for a substance B contained in it (Fig. 20.3). Take $c_{B,0}$ as the concentration of B at uniform distribution in the container. The concentration gradient is then $dc_B/dx = 2c_{B,0}/l$. At the first moment

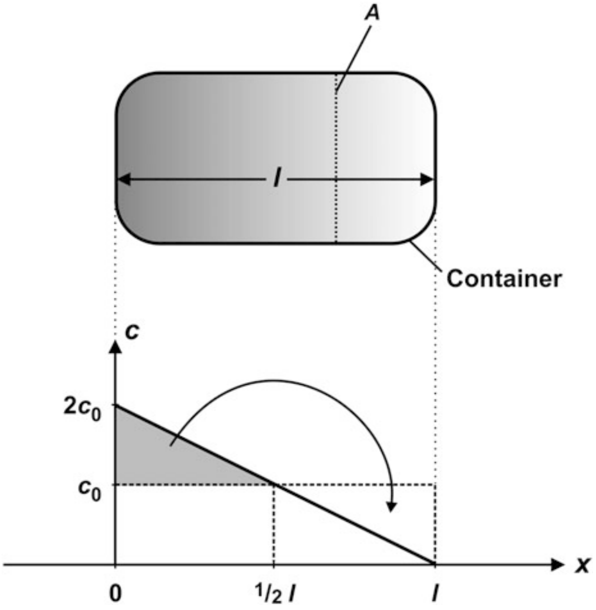


Fig. 20.3 Concentration equalization in a container in which a linear concentration gradient is initially assumed. To achieve equalization, it is enough to transfer the amount of substance $n = \frac{1}{2} \cdot c_0 \cdot (\frac{1}{2}l) \cdot A$ indicated by the *gray triangle* in the lower partial image from left to right.

t_0, the flux density j_B of B is the same everywhere. The diffusion law tells us that it is $j_B = D_B \cdot 2c_{B,0}/l$. We assume this value to remain unchanged for a cross section exactly through the middle of the container for a time span Δt. The amount of substance flowing through this cross section in this time span is then $\Delta n_B = A \cdot \Delta t \cdot j_B$. The amount of B flowing from left to right (in order to establish a uniform concentration) is indicated by the dark triangle in the figure. It is exactly ¼ of the amount of B in the container, $A \cdot l \cdot c_{B,0}$, that is represented by the large triangle. If Δn_B should equal this amount, then

$$\Delta n_B = A \cdot \Delta t \cdot j_B = A \cdot \Delta t \cdot D_B \frac{2c_{B,0}}{l} = \frac{1}{4} A \cdot l \cdot c_{B,0} \quad \text{and} \quad \Delta t = \frac{l^2}{8D}. \qquad (20.13)$$

Δt roughly represents the time needed to approximately equalize the concentration in the container. We see that the time decreases by l^2, becoming very short for small diffusion lengths. Hence, the differences in concentration equalize very quickly. This is why for small dimensions, diffusion is a very efficient method of distribution. We see it in the exchange of substances in living cells and in the equalization of residual differences of concentration after two different solutions have been stirred together.

Here is an example: In liquids, low-molecular substances have a diffusion coefficient of the order of 10^{-9} m^2 s^{-1}. In a red blood cell with a diameter of about 10^{-5} m, the time necessary for diffusion of these substances is approximately

$$\Delta t = \frac{l^2}{8D} = \frac{\left(10^{-5}\,\text{m}\right)^2}{8 \times 10^{-9}\,\text{m}^2\,\text{s}^{-1}} \approx 10^{-2}\,\text{s}.$$

In normal cells having a size of about 10^{-4} m, the time needed is $\Delta t \approx 1$ s, while in a 1 L glass beaker (diameter 10^{-1} m), 10^6 s $\approx$ 2 weeks are generally required. For this reason, stirring is necessary in order to homogenize solutions in large containers.

While the container mentioned above should be closed on all sides, let us now imagine a layer of thickness l so that a substance B can escape on either side. This may be a plastic foil from which a plasticizer gradually diffuses. Starting on the surface, the entire layer is gradually affected and a sinusoidal concentration profile quickly emerges (Fig. 20.4). This profile then flattens slowly until it finally

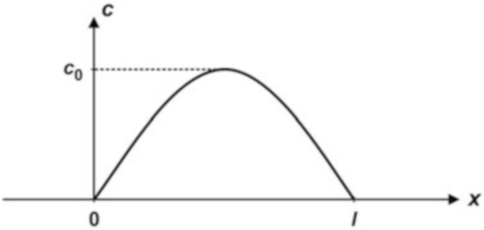


Fig. 20.4 Sinusoidal concentration profile on a layer open on both sides.

disappears altogether. At any position x, the concentration decreases exponentially with time t:

$$c_\mathrm{B} = c_{\mathrm{B},0} \sin \frac{\pi x}{l} \cdot e^{-t/\tau_1} \quad \text{with} \quad \tau_1 = \frac{l^2}{\pi^2 D_\mathrm{B}}. \tag{20.14}$$

The decay time τ_1 agrees with our estimate (20.13), but instead of the 8 in the denominator, we now have $\pi^2 \approx 9.9$. Any concentration profile can be represented by a superposition of such sinusoidal profiles that change independently of each other in the course of time. Profiles having a "wavelength" $\lambda_n = \lambda_1/n$ that is shorter by $1/n$ $(n = 1, 2, 3, \ldots)$ than that of the "fundamental wave" $\lambda_1 = 2l$ have a decay time $\tau_n = \tau_1/n^2$ that is shorter by the factor $1/n^2$ as we can see in Eq. (20.14). The corresponding theory was developed by the French mathematician and physicist Jean Baptiste Fourier at the beginning of the nineteenth century using heat conduction that obeys similar laws.

Diffusion Control Let us now return to the subject of Sect. 20.1. We wish to make a rough estimate of the rate density r for a reaction $\mathrm{A} + \mathrm{B} \rightarrow \ldots$, where the collision of two particles A and B is the step that determines the rate. For the sake of simplicity, we imagine the particles to be spheres where the type A is mobile and the type B is not. As soon as an A particle approaches a B particle (or more exactly, the centers of the particles) to a distance of a_0, a reaction is assumed to occur where A disappears. In the process, an A-poor environment is produced around B, which we will imagine as spherically symmetrical in shape and into which the A diffuses from the surroundings. If c_A^∞ is the concentration of A in the environment, meaning far away from B, the following equation should be valid for c_A in the depletion zone at a distance a from B:

$$c_\mathrm{A} = c_\mathrm{A}^\infty \cdot \left(1 - \frac{a_0}{a}\right) \text{ and therefore } \frac{\mathrm{d}c_\mathrm{A}}{\mathrm{d}a} = c_\mathrm{A}^\infty \cdot \frac{a_0}{a^2}.$$

This approach seems reasonable because for large a, c_A tends toward c_A^∞ and at a distance, $a = a_0$, we have $c_\mathrm{A} = 0$, because A disappears. On the other hand, the matter flux J_A out of the environment in the B direction must be independent of a for $a \geq a_0$ because A is neither formed nor destroyed under way. This applies to the approach above because according to Fick's law $j_\mathrm{A} = -D_\mathrm{A} \cdot (\mathrm{d}c_\mathrm{A}/\mathrm{d}a)$, we find for the flux J_A through the surface $4\pi a^2$ of a sphere with a radius a around the center of B:

$$J_\mathrm{A} = 4\pi a^2 \cdot |j_\mathrm{A}| = 4\pi a^2 \cdot D_\mathrm{A} \cdot c_\mathrm{A}^\infty \frac{a_0}{a^2} = 4\pi D_\mathrm{A} a_0 c_\mathrm{A}^\infty = \text{const.}$$

J_A multiplied by the number $N_\mathrm{B} = n_\mathrm{B}/\tau = c_\mathrm{B}^\infty V/\tau$ of all the B particles in a volume V yields the conversion rate ω. When we finally divide by V, the result is the desired rate density r:

$$r = k \cdot c_\mathrm{A}^\infty \cdot c_\mathrm{B}^\infty \ \text{ with } \ k = 4\pi D_\mathrm{A} \frac{a_0}{\tau}.$$

If B is also mobile, r will be somewhat greater, because $D_\mathrm{A} + D_\mathrm{B}$ will appear in the formula on the right instead of D_A. This detail is unimportant to our estimate, so we can omit it. According to Table 20.3, D is of the order of $10^{-9}\ \mathrm{m^2\ s^{-1}}$ for low-molecular substances in an aqueous solution, and a_0 corresponds to the particle diameters and is approximately 10^{-9} m. These values yield

$$k = 4\pi \times 10^{-9}\,\mathrm{m^2\,s^{-1}} \frac{10^{-9}\,\mathrm{m}}{1.66 \times 10^{-24}\,\mathrm{mol}} \approx 10^{7}\,\mathrm{m^3\,s^{-1}\,mol^{-1}}.$$

Compared to this, the k value for a bimolecular reaction (Sect. 18.3) with a vanishing activation threshold, $\Delta_{\ddagger}\overset{\circ}{\mu} = 0$, is 1,000 times greater:

$$k = \frac{k_\mathrm{B} T}{h c^{\ominus}} = \frac{1.38 \times 10^{-23}\,\mathrm{J K^{-1}} \times 300\,\mathrm{K}}{6.63 \times 10^{-34}\,\mathrm{J\,s} \times 10^{3}\,\mathrm{mol\,m^{-3}}} \approx 10^{10}\,\mathrm{m^3\,s^{-1}\,mol^{-1}}.$$

Only at an activation threshold $\Delta_{\ddagger}\overset{\circ}{\mu}$ considerably above $3\mu_\mathrm{d}$, does this step—rather than diffusion—determine the conversion rate.

Due to their larger particle diameters and decreased diffusion coefficients, high-molecular substances such as enzymes lead to considerably lower k values of the order of 10^5 to $10^6\ \mathrm{m^3\ s^{-1}\ mol^{-1}}$.

20.3 Fluidity

Viscosity Gases and liquids can flow more or less easily. Shear forces cause the particles to rub and slide against each other. The more viscous the liquid or gas is under equal driving forces.

- The lower the flow velocity and therefore for example the outflow velocity associated with it (Experiment 20.3),
- The slower the migration of dissolved substances in it (diffusion, sedimentation, ion migration).

Flow of substances is always hindered by inner friction. The driving force needs to overcome this resistive force. Let us imagine two parallel plates with surfaces of A at a set distance of d from each other. There is a gas or liquid between these plates acting as a kind of lubricant (Fig. 20.5). The upper plate is now passed over the stationary lower plate in the x direction at a constant speed v_0. If we were to look at

Experiment 20.3 *Outflow of various glycerin–water mixtures*: Three glycerin–water mixtures with different compositions are filled into separating funnels. The stopcocks are then quickly opened, one after the other. The lower the fraction of viscous glycerin, the faster the mixture flows out.

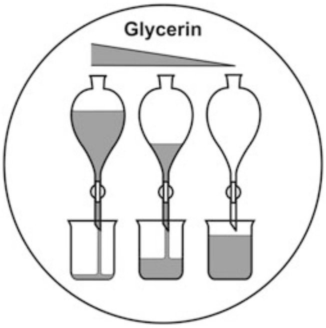
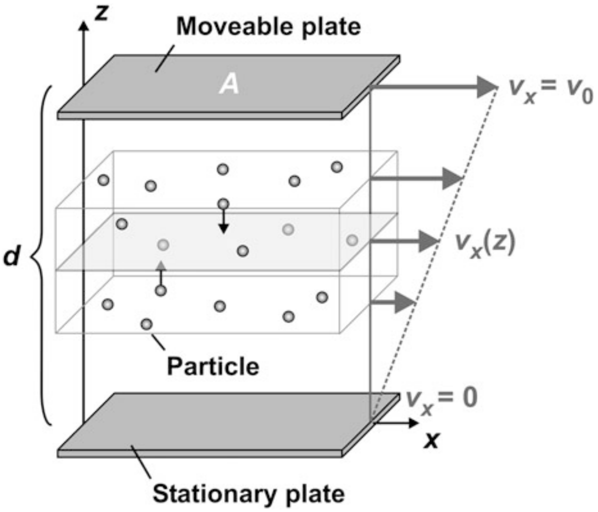


Fig. 20.5 Linear velocity profile of a liquid or, in this case, a gas between one moveable and one stationary plate. A change of particles between the layers is related to a momentum transport.



the liquid at microscopic scale, we would see that due to adhesion forces, its particles adhere to the plates in a thin layer. The particles are motionless on the stationary lower plate, while the particles on the upper plate are carried along at the speed v_0. The liquid lying in between can be imagined as divided into thin, flat layers where the speed will be higher, the closer it is to the upper plate. A linear velocity profile $v_x(z)$ emerges that is dependent upon the vertical distance z from the lower plate. A stack of glass plates held together by honey can serve as a model (Experiment 20.4).

The particles do not adhere to their original layer but can leave it by taking their p_x momentum (in the x direction) so that a transport of momentum takes place perpendicular to the direction of motion. When particles move from a lower to a higher layer, they will have a braking effect because they have a lower momentum in the x direction than the other particles. Conversely, an acceleration will occur due to particles moving down from a higher layer. These interactions are noticeable as

Experiment 20.4 *Honey experiment*: About ten glass plates (microscope slides, for example) are smeared with honey and then stacked one upon the other. The slow slide of the topmost plate leads to a movement by all of them (except the lowest one which is held in place).

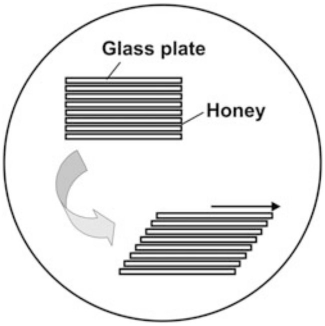


Table 20.4 Dynamic and kinematic viscosity, η and v ($= \eta/\rho$), of various substances at 293 K.

Substance	η (10^{-3} Pa s)	v (10^{-6} m^2 s)
Water	1.002	1.004
Mercury	1.526	0.115
Diethyl ether	0.243	0.340
Benzene	0.604	0.736
Ethylene glycol	19.9	17.9
Glycerin	1,412	1,120
Honey	~10^4	~10^4
Tar	$>10^5$	$>10^5$
Hydrogen	0.89×10^{-2}	106
Oxygen	2.03×10^{-2}	15.3

so-called *inner friction* (as opposed to outer friction between two solid bodies such as static friction and rolling friction where it is mostly only surfaces that are affected). The friction force F_f to be overcome is not only dependent upon the surface A, but also upon the transfer of momentum between the layers and therefore the velocity gradient $\Delta \upsilon_x/\Delta z$,

$$F_\mathrm{f} = -\eta \cdot A \cdot \frac{\Delta \upsilon_x}{\Delta z} \quad \text{Newton's law of friction (global form)}, \qquad (20.15)$$

where, in our case, we simply have $\Delta \upsilon_x/\Delta z = \upsilon_0/d$. The proportionality factor η is called the (dynamic) *viscosity*. It is a property of a substance and its SI unit is N s m^{-2} = Pa s. Table 20.4 contains viscosities for some substances at 293 K. In addition, the ratio $v = \eta/\rho$, the so-called *kinematic viscosity*, has been included. We will return to this further down.

A force F can be considered a momentum current (a flux of momentum) J_p (Sect. 2.7). Consider one-dimensional motion, say pushing a motor vehicle (Fig. 2.12). If p indicates the momentum of the object being moved and F is the only force acting upon it (i.e., if F is the only path over which the object exchanges momentum with its environment), we have:

$$F = J_p = \frac{\mathrm{d}p}{\mathrm{d}t} \quad \left(\text{for several paths we have}: \sum_i F_i = \sum_i J_{p,i} = \frac{\mathrm{d}p}{\mathrm{d}t}\right).$$

If we imagine momentum flowing via a straight rod having a uniform cross section of A into an object being pushed in the x direction, the *momentum current density* everywhere in the rod will equal $j_p = J_p/A$. The transport of momentum here occurs at the speed of sound, without loss and without energy being dissipated and entropy being generated.

The momentum transport we are interested in here differs in several ways from the one just discussed. It is not one-dimensional, so for vector quantities such as momentum and velocity we need to distinguish the components in the x, y, and z directions. In Fig. 20.4, these are the directions left to right, front to back, and bottom to top. Our case is comparably simple because only the x components p_x and v_x of momentum and velocity do not equal zero. Unlike before, the momentum is not conveyed in the x direction but perpendicularly to it, following the velocity gradient $\mathrm{d}v_x/\mathrm{d}z$, from top to bottom. The fact that we are dealing with the z-component of the flux of p_x may be expressed by notations such as $J_{px,z}$ or $(J_p)_{x,z}$. Since this is the only relevant component here, we can forgo the indices and simply write J_p, which is identical to the force appearing in Newton's law of friction (20.15). If we introduce this quantity or, rather, the related momentum flux density $j_p = J_p/A$ into the friction law, and replace the difference quotient $\Delta v_x/\Delta z$ by the differential quotient $\mathrm{d}v_x/\mathrm{d}z$, it turns into

$$j_p = -\eta \frac{\mathrm{d}v_x}{\mathrm{d}z} \quad \text{Newton's law of friction (local form).} \tag{20.16}$$

The velocity v_x appears here in the role of a potential belonging to the substance-like quantity momentum p_x. We describe it as "kinetic" or "kinematic" to distinguish it from other potentials such as the chemical potential μ or the "thermal potential" T.

Duration of Velocity Equalization If the upper plate is not constantly pushed forward giving it a constant supply of momentum p_x, the fluid flow between the plates will soon come to a stop. This also happens when the lower plate is not held so that momentum cannot flow off there. In this situation, the momentum behaves like a diffusing substance in a closed container. For the sake of simplicity, we will imagine the plates to have no mass so that they can adapt without inertia to the velocity of the adjacent layer of liquid. All that remains is the redistribution of momentum p_x in the liquid where the excess in the upper half is to be moved to the lower half. If ρ is the density of the liquid, mass (first term), average velocity (second term), and momentum (third term) are:

$$\begin{array}{llll} \text{above}: & \tfrac{1}{4}\,\rho \cdot A \cdot d, & \tfrac{3}{4}v_0, & \tfrac{3}{8}\,\rho \cdot A \cdot d \cdot v_0, \\ \text{below}: & \tfrac{1}{4}\,\rho \cdot A \cdot d, & \tfrac{1}{4}v_0, & \tfrac{1}{8}\,\rho \cdot A \cdot d \cdot v_0. \end{array}$$

In order to attain a uniform distribution, it is enough to relocate $\Delta p_x = {}^1\!/_8 \rho \cdot A \cdot d \cdot v_0$ from above to below. Having an initial velocity gradient of v_0/d, the amount $\Delta p_x = |j_p| \cdot A \cdot \Delta t = \eta \cdot (v_0/d) \cdot A \cdot \Delta t$ can be conveyed downward in the time span Δt. If we equate both Δp_x values and solve for Δt, we obtain a relation corresponding to Eq. (20.13) where ν is the *kinematic* viscosity mentioned above:

$$\Delta t = \frac{d^2}{8\nu} \quad \text{with} \quad \nu = \frac{\eta}{\rho}. \tag{20.17}$$

ν has the same SI unit as the diffusion coefficient D, namely $\mathrm{m^2\,s^{-1}}$. The statements above about concentration profiles and their decomposition into sinusoidal contributions and their decay times are correspondingly valid for velocity profiles $v_x(z)$.

Particles in a Viscous Medium In many examples, particles such as molecules or macromolecules or ions move in a medium having a viscosity of η. However, let us first consider the motion of a macroscopic sphere with radius r at a velocity of v in a liquid or gas. This motion is caused by a force such as the force of gravity. A frictional force acts against it and this force will be greater the more viscous the medium is and the larger the sphere. It also rises as velocity increases. From the field of hydrodynamics, we obtain

$$F_\mathrm{f} = 6\pi \cdot \eta \cdot r \cdot v \quad \text{Stokes' law.} \tag{20.18}$$

This equation can also be used approximately for microscopic particles like the molecules and ions mentioned above. We expect that the diffusion coefficient D_B of a substance B will be the smaller, the more viscous the medium is in which it migrates. Let us consider a simple example of a rigid, spherical particle with the radius r. The diffusion force [expressed by Eq. (20.1)] is counteracted by the Stokes frictional force [Eq. (20.18)]:

$$F_\mathrm{B} = \tau \cdot \frac{v_\mathrm{B}}{\omega_\mathrm{B}} = 6\pi \cdot \eta \cdot r_\mathrm{B} \cdot v_\mathrm{B} = F_\mathrm{f},$$

where $n_\mathrm{B} = \tau$ because we are only considering a single B particle, meaning an amount of substance B exactly corresponding to the elementary amount of substance τ. The result for mobility ω_B is then

$$\omega_\mathrm{B} = \frac{\tau}{6\pi \cdot \eta \cdot r_\mathrm{B}} \tag{20.19}$$

and because of $D_\mathrm{B} = \omega_\mathrm{B} RT$ (Einstein–Smoluchowski equation), the diffusion coefficient equals

$$D_\mathrm{B} = \frac{k_\mathrm{B} T}{6\pi \cdot \eta \cdot r_\mathrm{B}}, \tag{20.20}$$

where $k_B = \tau R$ is the Boltzmann constant. Because of this relation, we expect a temperature dependency for the viscosity of liquids which is the reciprocal of that of the diffusion coefficient [Eq. (20.12)]. If we take into account only the most important contribution, the exponential expression, we obtain:

$$\eta \sim \eta_\infty \cdot \mathrm{e}^{+W_A/RT}, \quad \text{where, for example,} W_A(H_2O) \approx 16\,\mathrm{kJ\,mol}^{-1}; \qquad (20.21)$$

therefore, we should expect a temperature dependency for the viscosity of liquids which is the reciprocal of that of the diffusion coefficient [Eq. (20.12)].

Viscosity should strongly reduce as temperature rises. Boiling water has four times lower viscosity than water at room temperature, allowing it to run correspondingly faster through a filter. This is good for laboratory work as well as making coffee.

20.4 Entropy Conduction

Entropy Conductivity Most of our experiences of entropy are gained in everyday life, even if unconsciously. The coffee in a thermos remains hot because it is difficult for entropy to penetrate the vacuum jacket, while coffee in a cup cools down fairly quickly because entropy leaves along with the steam rising from it. Gases and foam materials whose volumes are up to 97 % gas-filled pockets strongly hinder the flow of entropy, while metal exhibits a conductivity of about 1,000 times that much. We will quantify this phenomenon in the following (Fig. 20.6).

We will consider the simplest case, a *homogeneous*, *isotropic* body with a constant cross section A. Isotropic means that—in contrast to a block of wood, for example—all the directions are equal. If the temperature drops from left to right, entropy moves in this direction. Because most substance properties more or less depend upon temperature, and this is also true for the quantity that interests us here, we will only consider a small temperature difference $\Delta T \ll T$ between the left and right sides of the body. The entropy flux (or current) J_S or the entropy flux

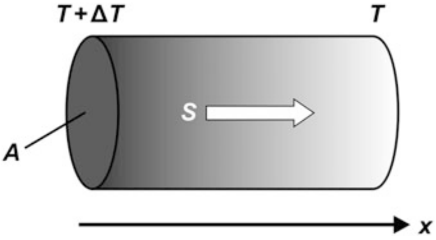
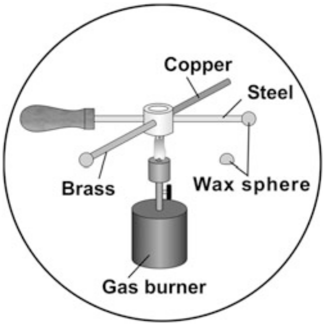


Fig. 20.6 Entropy conduction.

Table 20.5 Entropy conductivity σ_S and thermal conductivity λ at room temperature, when not otherwise indicated.

Substance	σ_S (Ct $\mathrm{K^{-1}\ s^{-1}\ m^{-1}}$)	λ (J $\mathrm{K^{-1}\ s^{-1}\ m^{-1}}$)
Diamond	8	2,300
Copper	1.3	400
Brass (40 % Zn)	0.2	113
Stainless steel	0.05	15
Glass	0.003	0.8
Water (0 °C)	0.00205	0.56
Water (100 °C)	0.00182	0.68
Foam materials	0.00015	0.04
Air	0.000087	0.026



Experiment 20.5 *Entropy conduction in solid substances*: A cross made of a copper rod, a brass rod, and a steel rod with wax spheres attached to their ends is heated in the middle. The wax spheres fall off one after another according to the different entropy conductivities: first copper, then brass, and finally, steel.

(or current) density $j_S = J_S/A$ are proportional to the temperature gradient $\Delta T/\Delta x$ or more precisely $\mathrm{d}T/\mathrm{d}x$:

$$J_S = \sigma_S \cdot A \cdot \frac{\Delta T}{\Delta x} \quad \text{or} \quad j_S = -\sigma_S \cdot \frac{\mathrm{d}T}{\mathrm{d}x} \quad \text{Fourier's law.} \tag{20.22}$$

These are two simple versions, a global one and a local one, of a law mentioned at the end of Sect. 20.2 for which Fourier introduced solution methods in 1822 which have proven applicable to many areas of physics and mathematics. σ_S is the entropy conductivity. Instead of σ_S, in tables we usually find the entropy conductivity multiplied by T, the "heat conductivity" (or thermal conductivity) $\lambda = T \cdot \sigma_S$. Table 20.5 contains some values for these two quantities.

The example of water shows us that neither λ nor σ_S can be considered constant. In the case of monoatomic or biatomic gases such as air, σ_S changes in proportion to $T^{-1/2}$ and therefore $\lambda \sim T^{+1/2}$. This dependency is mostly neglected because any mistakes involving it are unimportant compared to other less controllable influences.

Let us take a look at an experiment showing different entropy conductivities in various solid substances (Experiment 20.5).

Duration of Temperature Equalization When making a boiled egg for breakfast we want to know how long it needs to boil to reach the soft or hard consistency that we desire. This question is similar to the one about how long it takes for an equalization of concentration to be achieved in a closed container (Fig. 20.3). We will refer to the same image, but will now plot temperature T instead of concentration c along the ordinate. In place of the equalized concentration c_0 obtained in the end, we have the corresponding temperature T_0. We assume a linear temperature gradient where, on the far left, we have a temperature of $T_0 + \Delta T$, and on the far right, $T_0 - \Delta T$, with $\Delta T \ll T$. The gray triangle on the left corresponds to an excess of entropy of $\Delta S = \frac{1}{2}\, \mathcal{C} \cdot \frac{1}{2} \Delta T$ in the left part of the body and for which there is a corresponding lack of entropy on the right. $\mathcal{C}$ is the entropy capacity $\mathcal{C} = m \cdot \boldsymbol{c}$ of the entire body, $m = \rho \cdot A \cdot l$ its mass, ρ is the density, and $\boldsymbol{c} = \mathcal{C}/m$ the *specific* entropy capacity. While $\mathcal{C}$, A, l, and m are characteristics of the body, ρ and $\boldsymbol{c}$ indicate properties of the substance it is made up of. In summary:

$$\Delta S = \frac{1}{2}\, \mathcal{C} \cdot \frac{1}{2}\, \Delta T = \frac{1}{4} \boldsymbol{c} \rho A l \cdot \Delta T.$$

If we imagine a constant temperature gradient of $2\Delta T/l$, then an amount of entropy equal to

$$\Delta S = J_S \Delta t = \sigma_S \cdot A \cdot \frac{2\Delta T}{l} \Delta t$$

will flow from left to right during the short time span Δt (see Fourier's law [Eq. (20.22)]. If we equate both ΔS values and solve for Δt, we obtain an approximate value for the duration of temperature equalization:

$$\Delta t = \frac{l^2}{8a} \quad \text{with} \quad a = \frac{\sigma_S}{\rho \boldsymbol{c}} = \frac{\lambda}{\rho c_\mathrm{s}}. \tag{20.23}$$

The coefficient a in the denominator is called the "temperature conductivity," although this is somewhat misleading because it is not the temperature which is conducted. In the formula on the right, a is not only expressed by the entropic quantities σ_S and $\boldsymbol{c}$, but also by their energetic opposites λ and c_s, thermal conductivity and specific heat capacity. (We use the symbol c_s instead of the usual c to avoid any confusion with the symbol c for concentration.)

Coupling of Matter and Entropy Currents What happens when a substance is simultaneously subjected to a gradient of its potential μ and the temperature T? Let us imagine a pond where the water below is cold, T_1, and heats up in the Sun becoming warm above with $T_2 > T_1$. Then $\mu_2 = \mu_1 + \alpha \cdot (T_2 - T_1) < \mu_1$ would be the case because $\alpha = -S_\mathrm{m}$ is negative. Consequently, there is a drive for water to rise upward. The entropy in the water strives downward, and in the process, both influences cancel each other. The amount of energy $W_n + W_S$ expended for shifting an amount of water n upward is:

$$W_n + W_S = (\mu_2 - \mu_1)n + (T_2 - T_1)S = -S_\mathrm{m}(T_2 - T_1)n + (T_2 - T_1)S_\mathrm{m} \cdot n = 0.$$

This is not always the case. When a dissolved substance diffuses, the molar entropy carried along with it, the so-called transfer entropy S_m^*, is greater or smaller than S_m. S_m^* is about 2.7 Ct mol^{-1} greater in a cane sugar solution with a concentration of 1 kmol L^{-1}. The influence of entropy gains the upper hand here so the sugar is forced to the cooler side. At a temperature difference of 10 K, and an enrichment of about 1.1 %, the two effects just compensate for each other. Let us calculate the energy expenditure for the transport of a small amount of sugar n from the cooler side, T_1, to the warmer side, $T_2 > T_1$:

$$\begin{gathered} W_n + W_S = (\mu_2 - \mu_1) \cdot n + (T_2 - T_1) \cdot S_\mathrm{m}^* \cdot n, \\ = \left[\left(\left(\mu_1 - S_\mathrm{m}(T_2 - T_1)\right) - (\mu_1 + RT_1 \ln 1.011) + (T_2 - T_1)S_\mathrm{m}^*\right] \cdot n, \\ = \left[\left(S_\mathrm{m}^* - S_\mathrm{m}\right)(T_2 - T_1) - RT_1 \ln 1.011\right] \cdot n, \\ = \left[2.7\,\mathrm{Ct\,mol^{-1}} \times 10\,\mathrm{K} - 8.3\,\mathrm{Ct\,mol^{-1}} \times 300\,\mathrm{K} \times \ln 1.011\right] \cdot n = [27 - 27] \cdot n = 0. \end{gathered}$$

Differences in the chemical potential caused by a temperature gradient are called *thermodiffusion*, whereas the inverse effect where temperature differences are caused by a gradient of the chemical potential is called the *diffusion-thermo effect*. Such couplings between currents are common. The most well known is the *thermoelectric effect* which is caused by a coupling of entropy and charge currents.

20.5 Comparative Overview

Transport Equations In order to carve out the commonalities and differences of the phenomena we have discussed, we will sum them up here. In doing so, we will add another phenomenon: transport of electric charge (Fig. 20.7), because it is the best known of these. Its concepts can serve as an example or help in orientation. In all four cases, diffusion, viscous flow, entropy conduction, and conduction of electricity, there is a substance-like quantity (substance B, momentum p_x, entropy S, and charge Q) being conveyed along the gradients of the corresponding potentials (chemical μ_B, "kinetic" v_x, "thermal" T, and electric φ). In order to look at all this uniformly, we can imagine a small cuboid shaped section of a larger area with the base area A and the height l. The height should be so small that despite an assumed potential difference, the cuboid can be considered homogeneous.

A drop in potential of $\Delta\mu_\mathrm{B}$, Δv_x, ΔT, $\Delta\varphi$ from the upper surface to the lower surface drives a current of J_B, J_p, J_S, J_Q downward through the cuboid as long as there is a corresponding conductivity σ_B, σ_p, σ_S, σ_Q to allow for this. The current is proportional to the cross section A and the potential difference and inversely

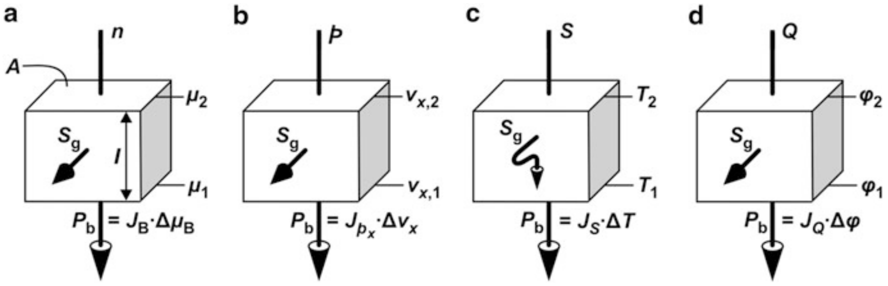


Fig. 20.7 Comparison of different transport processes: (**a**) substance, (**b**) momentum, (**c**) entropy, (**d**) charge. P_b is the dissipation rate, $\dot{S}_g = P_b/T$ the generation rate of entropy, if T is the instantaneous average temperature of the body. In the case of (**c**), the generated entropy leaves along the same path as the one entering from above (indicated by the *arrow bending backward*).

Table 20.6 Comparison of related formulas for different transport processes.

	Diffusion (Fick)	Viscous flow (Newton)	Entropy conduction (Fourier)	Electric conduction (Ohm)
Global form	$J_B = -\sigma_B \cdot A \frac{\Delta\mu_B}{l}$	$J_{px} = -\sigma_p \cdot A \frac{\Delta v_x}{l}$	$J_S = -\sigma_S \cdot A \frac{\Delta T}{l}$	$I = -\sigma \cdot A \frac{\Delta\varphi}{l}$
Local form	$j_B = -\sigma_B \cdot \frac{d\mu_B}{dz}$	$j_{px} = -\sigma_p \cdot \frac{dv_x}{dz}$	$j_S = -\sigma_S \cdot \frac{dT}{dz}$	$j = -\sigma \cdot \frac{d\varphi}{dz}$
Special form (example)	$j_B = -D_B \cdot \frac{dc_B}{dz}$	$F_f = -\eta \cdot A \cdot \frac{dv_x}{dz}$	$J_Q = -\lambda \frac{dT}{dz}$	$I = \frac{U}{R_Q}$
Conductivity	$\sigma_B = c_B D_B / RT$	$\sigma_p = \eta$	$\sigma_S = \lambda / RT$	$\sigma = 1/\rho_Q$
"Diffusivity"	D_B	$v = \eta/\rho$	$a = \lambda/(c_s \rho)$	–

The formulas in the first line are analogous to each other as are the ones in the second line. In the third line, they are adapted to special applications and contain quantities that only correspond to each other to a certain extent. In the fourth line the "conductivities" and in the fifth line the corresponding "equalization coefficients" ("diffusivities") are expressed by the preferred quantities of their respective domains. (The index Q in the fourth row corresponds to "heat" and in the fifth row, however, to "charge")

proportional to the length l through which the current flows whereby the conductivity σ_B, σ_p, σ_S, σ_Q appears as a proportionality factor. The formulas have been compiled in Table 20.6, where in the case of charge, the usual symbols I, j, and σ have been used instead of J_Q, j_Q, and σ_Q. The names of the persons for whom these laws have been named are at the top of the table. In the line below that are the analogous "local" laws in which the current J is replaced by the corresponding current density $j = J/A$ and the quotient "potential difference/length" is formulated as the derivative of the potential in question with respect to the spatial coordinate z.

The most well-known version of *Ohm's law* is $I = U/R_Q$, where I generally means "current," $U = -\Delta\varphi$ "voltage," $R_Q = \rho_Q \cdot l/A$ "(electric) resistance," and $\rho_Q = 1/\sigma$ "(electric) resistivity." The "conductance" $G_Q = 1/R_Q$ is often used instead of R_Q, which gives Ohm's law the following form: $I = G_Q \cdot U$. For clarity's sake, we have included the index $_Q$ because we are already using the symbols without indexes for other purposes. There is a comparable diversity for the formulas in the other columns, so it is difficult to find their common pattern. To give an example, the inverse $\varphi = \eta^{-1}$ of the viscosity η is in use as well. It is called *fluidity* and corresponds to the resistivity ρ_Q.

"Diffusivities" Despite their very different names, the "diffusion coefficient" D_B, the "kinematic viscosity" ν, and the "temperature conductivity" a are analogous quantities. They all have the SI unit $\mathrm{m}^2\ \mathrm{s}^{-1}$ and quantify properties of substances with respect to different transport processes that determine the durations of equalization processes. They are called *diffusivities* (or "*equalization coefficients*").

They can be written as the quotient "conductivity/capacity density," as would be expected. The more conductive the medium, the more quickly the potential differences equalize. The larger the amount to be transported, i.e., the higher the capacities at equal potential differences, the longer it will take. Because $\sigma_\mathrm{B} = c_\mathrm{B}\omega_\mathrm{B}$ describes the "matter conductivity" [Eq. (20.6)] and $\text{б}_\mathrm{B} = \mathrm{c}_\mathrm{B}/RT$ the "matter capacity density" (Sect. 6.7), the following is valid:

$$D_\mathrm{B} = \omega_\mathrm{B}RT = \frac{\omega_\mathrm{B}c_\mathrm{B}}{c_\mathrm{B}/RT} = \frac{\sigma_\mathrm{B}}{\text{б}_\mathrm{B}} = \frac{\text{“matter conductivity”}}{\text{“matter capacity density”}}.$$

In the case of momentum, the mass $m = \rho \cdot V$ plays the role of "capacity" and because $p_x = mv_x$, taking the derivative with respect to the proper "potential" v_x simply results in $\mathrm{d}p_x/\mathrm{d}v_x = m$. The corresponding "capacity density" is therefore the mass density $m/V = \rho$. Viscosity η corresponds to momentum conductivity σ_p, so the following holds:

$$\nu_\mathrm{B} = \frac{\eta}{\rho} = \frac{\text{“momentum conductivity”}}{\text{“momentum capacity density”}}.$$

In Eq. (20.23) for the temperature conductivity (thermal diffusivity) $a = \sigma_S/(\rho \cdot \mathcal{c})$, $\mathcal{c}$ indicates the specific or entropy capacity per mass and $\rho \cdot \mathcal{c}$ is the corresponding volumic quantity, the corresponding "capacity density," so that:

$$a = \frac{\sigma_S}{\rho\mathcal{c}} = \frac{\text{“entropy conductivity”}}{\text{“entropy capacity density”}}.$$

Accompanying Energy Currents Each of the currents J_B, J_p, J_S, J_Q is accompanied by an energy current $J_W = \mu_\mathrm{B} \cdot J_\mathrm{B}$, $J_W = v_x \cdot J_p$, $J_W = T \cdot J_S$, $J_W = \varphi \cdot J_Q$. More energy flows in than flows out because the potentials at the inflow are higher than at the outflow. The excess energy could be used for other purposes if there were an apparatus for doing so. This does not happen here. Instead, as the energy is dissipated while entropy is generated, the energy is lost or becomes "useless." The *dissipation power* P_b (the part of the energy current that is dissipated or "burnt") is given in Fig. 20.7 for the cases illustrated there. If T is the temperature, the generation rate of entropy resulting from it is:

$$\dot{S}_{\mathrm{g}} = \frac{P_{\mathrm{b}}}{T}.$$

If this entropy is not drawn off, the body will heat up continuously. However, if the entropy is allowed to flow away at a constant temperature T, energy, namely P_{b}, will also flow off along the same path. The energy current then bifurcates as part of it flows out with the entropy S_{g}.

This looks a little different in case c of Fig. 20.7, because the entropy S_{g} generated there flows away along the same path as the one flowing in above. While the entropy continually grows as it moves through the temperature gradient, the energy remains the same. For this reason, there is a preferred description of this case in which the energy itself is considered the flowing substance. The corresponding current density $j_W = T \cdot j_S$ is obtained by multiplying Eq. (20.22) for entropy by the temperature T, where we also replace $T \cdot \sigma_S$, as is usual in this case, by λ:

$$J_W = \lambda \cdot A \cdot \frac{\Delta T}{\Delta x} \quad \text{or} \quad j_W = -\lambda \cdot \frac{\mathrm{d}T}{\mathrm{d}x} \quad \text{“heat conduction equation”}. \tag{20.24}$$