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Understanding Diffusion and Demonstrating it Correctly – A Critical Look at a Transport Process often Incorrectly Taught in Schools

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Abstract Diffusion is a transport process frequently shown experimentally in beginning science classes. However, quite a few standard school “diffusion experiments” such as letting food colorant drip into water and spraying perfume (or similar) into a classroom provide a false picture of diffusion by demonstrating convection, transport by flow, instead. The article explains why these two standard experiments clearly show convection and should therefore be banned from school lessons as "diffusion experiments": Diffusion is explained to be an entropy-driven process and, based on this, the so-called EINSTEIN-SMOLUCHOWSKI equation is derived with the help of simple probability calculations. Using the EINSTEIN-SMOLUCHOWSKI equation, it is then shown how transport phenomena can be clearly recognized as diffusion or be unmasked as convection experiments. The reader is provided with alternative *genuine* diffusion experiments for beginning classes that *verifiably* demonstrate diffusion, namely the spread of ammonia and hydrogen chloride in a sealed glass tube and the spread of methylene blue in water-based gels. Additionally, it is shown how these experiments can be used to quantify diffusion constants with the aid of the EINSTEIN-SMOLUCHOWSKI equation.

Keywords: *diffusion, misconceptions, convection, school experiments, laboratory computing*

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1. Introduction

Diffusion describes a physical transport process of matter that is not only of particular significance in cell physiology [1] and in electrochemistry (especially in the context of voltammetry and chronoamperometry [2]), but with the help of which EINSTEIN and SMOLUCHOWSKI found one of the strongest proofs for the existence of molecules [3].

Diffusion is usually discussed in beginning science (chemistry, biology, physics) classes and *qualitative* demonstrations are *attempted*. However, it often remains an *attempt*, as some experiments teachers may have grown fond of are clearly *no* diffusion experiments, but show so-called convection, a flow-induced transport phenomenon instead [4,5]: In this way, two experiments just have made it into the curriculum almost by default as “diffusion experiments”, namely letting food colorant drip into water and spraying perfume or similar into a classroom: The spread of the easily perceptible colorants or odorants is commonly interpreted as diffusion – a typical misconception that is found in literature again and again [4]. Even though there have already been efforts to banish these cherished experiments from the school curriculum in the past, e.g. [5] and also more recently, e.g. [6,7], these experiments continue to be carried out nonetheless. One reason for this may be that diffusion as such is often poorly understood and there is no overview for teachers of what diffusion actually is, what drives it and what mathematical relationships apply to it. There is also often a lack of well-justified alternatives to the experiments in question. The following article aims to change this.

2. Theory

2.1. The Driving Force of Diffusion

Suppose we have a cylinder containing a gas like methane whose pressure and temperature just correspond to atmospheric pressure and room temperature. If the cylinder is opened in an empty classroom, methane is distributed by diffusion until it is evenly mixed with air in the room. The diffusion-induced mass transport, which is associated with a concentration equalization, occurs from the place of higher to the place of lower concentration [1,8]. When the concentration gradient is eliminated, the diffusion flow comes to a standstill.

The concentration gradient implies a gradient of the chemical potential. We can interpret the chemical potential μ_i of a substance i as the molar free enthalpy G of a substance at constant temperature and constant pressure. If the chemical potential of a substance i differs in a phase, this substance is spontaneously transported from the location of the higher potential to the location of the lower potential until the chemical potential has the same value in all parts of the system. This case corresponds to $\Delta G=0$ and thus the state of equilibrium [9]. Equation 1 implies to the change in GIBBS energy [8]:

$$\Delta G = \Delta H - T\Delta S \tag{1}$$

If we consider ideal gases that mix with each other, then by definition the gas particles do not interact with each other, the enthalpy of mixing ΔH is therefore zero. The entire driving force of the mixing process thus results from an entropy increase (ΔS>0) [8]. The maximization of the mixing entropy is also a driving force in the diffusion of real gases. This can be understood particularly well according to the entropy definition in equation (2), in which k_B stands for the BOLTZMANN constant and W for the number of possibilities to arrange particles in a certain state of the system, more precisely the number of microstates that result in a certain macrostate [8,10,11].

$$S = k_B \ln W \tag{2}$$

Let's think back to the cylinder filled with methane: when the vessel is opened, methane mixes with air and the spatial inhomogeneity is eliminated by diffusion. Let's just imagine four methane molecules that are only allowed to move vertically in a tiny, closed space, i.e. upwards or downwards along an imaginary center line. The molecules enter many different microstates (one box each) equally often, some of which are shown in Figure 1. These microstates can be combined into different macrostates, which are all equivalent: For example, the combination "three molecules at the bottom, one molecule at the top" form four microstates that result in the same macrostate [11].

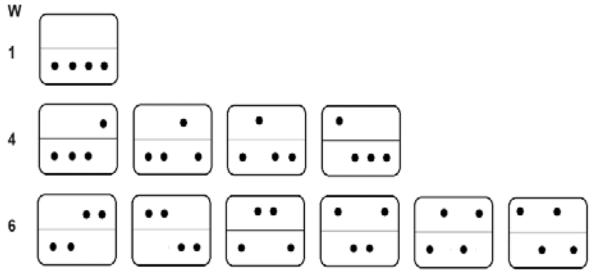

Figure 1. Microstates (box) of four molecules that form different macrostates (rows) [11]

As can be seen from the simple example, the macrostate that has the most microstates of equal value (possible combinations W) is the one in which the molecules are all evenly distributed [11]. The greater W is, the greater the entropy S according to Eq. 2. In other words, the greater the entropy is, the more probable the corresponding state. The most probable state, the state of uniform distribution, therefore always has the greatest entropy [10]. If there are many particles in a certain place, it is therefore very likely that they will be displaced from there[1]. Only in the long run, the random, undirected movements of the gas particles lead to a concentration equalization [1,12], i.e. complete mixing. Diffusion is therefore a stochastic process and can be described using probability theory [12]. This applies not only to the gaseous phase, but also to the liquid or solid phase [3].

2.2. Describing Diffusion Using Probability Theory

According to the MAXWELL-BOLTZMANN velocity distribution, the average speed of gaseous particles at room temperature is several 1000 kmh^{-1} [13]. Without an obstacle (i.e. in a vacuum), a gaseous molecule such as a methane molecule would be able to pass through a typical classroom in less than 1 second. However, diffusion does not occur at this speed, as the particles do not travel far before they collide with other particles [14]: Due to the collisions with other molecules – we are talking about several billion collisions per second (!) [8] – they are subject to a constant change of direction [13]. In this way, they are forced to move around in a constant zigzag motion, the so-called *random walk* [14].

In the following, this *random walk* will be described mathematically using simple probability calculation according to BERG [14]: We reduce the problem to the bare essentials and turn the three-dimensional problem into a one-dimensional one. Then, we consider the diffusion propagation of (methane) particles along only *one* axis. Each particle should overcome a step with the path length $\lambda = v_x\tau$ within the time τ with the average velocity v_x before a collision occurs and it changes its direction (in the direction of x or in the opposite direction). The probability is the same for a step to the left or to the right (p = ½). If a particle has moved from the origin to the right by $+\lambda$, in the next step it can either return to the origin $x = 0$ or move in the positive x-direction to $+2\lambda$ with the same probability in each case. We want to designate the position of a particle (named i) after the n^{th} step as $x_i(n)$. It reached this position from the previous position (= $x_i(n\text{-}1)$) by moving by $\pm\lambda$. Equation 3 therefore applies in general [14].

$$x_i(n-1) \pm \lambda = x_i(n) \tag{3}$$

λ can be interpreted as the so-called mean free path [15], i.e. the distance travelled by a particle between two collisions [13]. For simplicity, we treat λ and τ as constants. Furthermore, we assume that the particles do not interact and move independently of each other [14]. The case is shown in Figure 2 for the three-dimensional and the simplified one-dimensional *random walk*, see [16].

Finding a particle after, for example, $t = 3\tau$ ($n = 3$) at $x = +\lambda$ can be determined using a tree diagram (see Figure 2: 1D *random walk*): The probability for this is obtained by adding the probabilities along the paths that lead to this shift, in the case mentioned therefore by the combinations left-left-right, right-left-left and left-right-left and thus 3 · ½ · ½ · ½ = 3/8. If at the beginning $N = 80$ particles were located at x=0, this means that at the said time 30 particles are located at x=+λ. At the same time, 30 of the 80 particles are at x=-λ and 10 each at x =+3λ and x = -3λ. A closer look shows that the number of possibilities (denominator of the probability) of finding a particle at a

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[1] I would like to thank Dr. Thomas KRASKA, University of Cologne, for this vivid picture (personal communication).

certain position after n steps is given by the binomial coefficient, which can be read directly from the PASCAL triangle. Overall, the probability of finding a particle i at a certain position is binomially distributed. The typical bell curve is obtained for the probability. The distribution around x =0 is symmetrical (see Figure 2) [14,15,16].

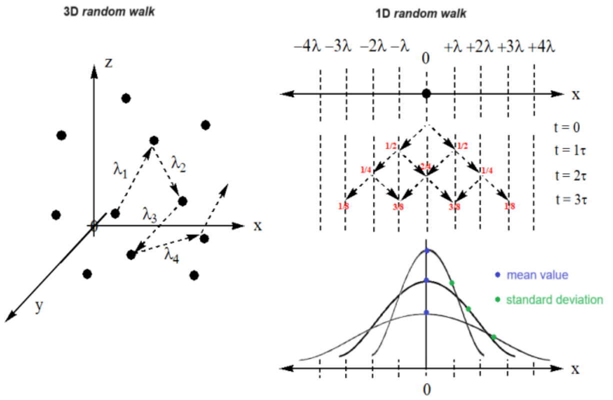

Figure 2. 3D *random walk* (left); simplified 1D *random walk* with indication of the probabilities for particle displacements after n = 3 steps (right) (cf. [16])

In order to calculate where the particles spread to *on average*, it may seem intuitive to calculate the mean value of all particle displacements. However, the mean value $\bar{x}(n)$ is always zero, as can easily be seen from the distances binomially distributed around the value 0 (see Figure 2): Figuratively speaking, the particles therefore do *not* move *on average* [14]. The mean value of the displacements, which apparently equals zero, can be obtained by multiplying the displacements $x_i(n)$ of all particles by their absolute frequency ($H_n(x_i)$) [17], then adding them together and dividing by the total number of particles N (Equation 4).[2] This is shown as an example in Tab. 1 for an ensemble of N = 80 particles after $t = 3\tau$.

Table 1. Diffusion-related distribution after n = 3 steps of N = 80 particles

displacement value $x_i(3)$	-3 λ	- λ	+ λ	+3 λ	
absolute frequency $H_3(x_i)$	10	30	30	10	$\Sigma H_3(x_i) = 80$
$\bar{x}(3)$	1/80 · [(-3 λ) · 10 + (- λ) · 30 + λ · 30 + 3λ · 10] = 0				

We write in general:

$$\bar{x}(n) = \frac{1}{N}\sum_{i=1}^{N} x_i(n) \cdot H_n(x_i) = 0 \qquad (4)$$

More helpful than the mean value $\bar{x}(n)$ is the standard deviation σ or its square σ^2. Both variables are a measure of the scattering or distribution of the individually observed values around the mean value. To calculate σ^2, the mean value is subtracted from all observed values $x_i(n)$ and the result is squared so that only positive values are obtained. The resulting value is again multiplied by the absolute frequency $H_n(x_i)$ (Equation 5) [14,17].

$$\sigma^2(x) = \langle x(n)^2 \rangle = \frac{1}{N}\sum_{i=1}^{N} (x_i(n) - \bar{x}(n))^2 \cdot H_n(x_i) \qquad (5)$$

Since $\bar{x}(n)$ is always zero for the considered diffusion case, the equation can be simplified to Equation 6.

$$\langle x(n)^2 \rangle = \frac{1}{N}\sum_{i=1}^{N} x_i(n)^2 \cdot H_n(x_i) \qquad (6)$$

We now use the relationship derived in Equation 3 for $x_i(n)$ and square it according to the rules of the first or second binomial formula ($(a \pm b)^2 = a^2 \pm 2ab + b^2$; whereby $a = x_i(n-1)$, $b = \lambda$). We obtain equation 7 [14]:

$$\begin{aligned}\langle x(n)^2 \rangle &= \frac{1}{N}\sum_{i=1}^{N} [x_i(n-1) \pm \lambda]^2 \cdot H_n(x_i) \\ &= \frac{1}{N}\sum_{i=1}^{N} [(x_i(n-1))^2 \underbrace{\pm 2(x_i(n-1))\lambda}_{=0} + \lambda^2] \cdot H_n(x_i) \qquad (7)\end{aligned}$$

The term $\pm 2(x_i(n-1))\lambda$ is zero, as the sign of λ is positive for one half of all particles and negative for the other half, so that they cancel each other out. Then, we factor out the remaining expression and write it in separate sums [14]. Note that the sum of all absolute frequencies corresponds exactly to N (see table 1). This gives us Equation 8.

$$\begin{aligned}\langle x(n)^2 \rangle &= \frac{1}{N}\sum_{i=1}^{N} [(x_i(n-1))^2 + \lambda^2] \cdot H_n(x_i) \\ &= \frac{1}{N}\sum_{i=1}^{N} [(x_i(n-1))^2 \cdot H_n(x_i) + \lambda^2 \cdot H_n(x_i)] \\ &= \underbrace{\frac{1}{N}\sum_{i=1}^{N} (x_i(n-1))^2 \cdot H_n(x_i)}_{cf.\,equation(6)} + \lambda^2 \cdot \frac{1}{N}\underbrace{\sum_{i=1}^{N} H_n(x_i)}_{=N} \\ &= \langle (x(n-1))^2 \rangle + \lambda^2 \qquad (8)\end{aligned}$$

The standard deviation of x after n steps equals the sum of the standard deviation of x of the previous step n-1 (see equation (6)) and λ^2. Since $x(0)=0$ applies to all particles – at time 0, i.e. after 0 steps, all particles are at the origin – the standard deviation after 0 steps (= $\langle x(0)^2 \rangle$) equals 0. Therefore, we obtain $\langle x(1)^2 \rangle = \langle x(0)^2 \rangle + \lambda^2 = \lambda^2$, if we insert n=1 into equation (8). If we put n = 2 into the equation and take the previous result into account, we obtain $\langle x(2)^2 \rangle = \langle x(1)^2 \rangle + \lambda^2 = \lambda^2 + \lambda^2 = 2\lambda^2$ and so on. In general, this results in equation 9 [14]:

$$\langle x(n)^2 \rangle = n\lambda^2 \qquad (9)$$

As originally described, a total of n steps take place within the time $t = n\tau$, i.e. $n = t/\tau$. We therefore rewrite equation 9 as a function of time and obtain equation 10 [14]:

$$\langle x(t)^2 \rangle = \frac{t}{\tau}\lambda^2 = \frac{\lambda^2}{\tau}t = 2\frac{\lambda^2}{2\tau}t = 2Dt \qquad (10)$$

For the sake of simplicity, the constant D is defined as $\lambda^2/2\tau$ so that the equation agrees with the numerous other derivations that exist [14]. For more detail please see [14].

The relationship obtained is known as the EINSTEIN-SMOLUCHOWSKI equation. Figuratively speaking, it indicates the distance of a particle cloud propagating from the origin, where x = σ applies. As the bell curve becomes flatter and flatter with time due to the propagation, σ also

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[2] For teachers: The same method is used to calculate the average grade of a test.

becomes larger and larger as a function of time and thus shows us the progress of diffusion as a function of time (see Figure 2) [14,18].

The made simplifications apply to *every* spatial dimension, i.e. not only for the *x*-axis, but also for the *y*- and *z*-axis: If $\langle x(t)^2\rangle = 2Dt$, then $\langle y(t)^2\rangle = 2Dt$ and $\langle z(t)^2\rangle = 2Dt$. We can think of movement in two or three dimensions as a combined movement in the *x*, *y* and *z* directions. Therefore, we can generally write equation 11 [14] for the time-dependent diffusion path *s*(*t*) as a function of the spatial dimension υ:

$$\langle s(t)^2\rangle = 2Dt + ... + 2Dt = \nu \cdot 2Dt \qquad (11)$$

Accordingly, $\langle (x(t),y(t))^2\rangle = 4Dt$ results for the two-dimensional case ($\upsilon = 2$) and $\langle (x(t),y(t),z(t))^2\rangle = 6Dt$ for the three-dimensional case ($\upsilon = 3$).

3. Diffusion Experiments at School

3.1. Unmasking Typical School "Diffusion Experiments" as Convection Experiments

From the EINSTEIN-SMOLUCHOWSKI equation derived in the previous chapter, an important key characteristic of the diffusion-induced transport process can be deduced, with which the "diffusion experiments" mentioned at the beginning can be identified as false already macroscopically: The diffusion time increases with the square of the distance travelled (($t \sim s(t)^2$). A doubling of the diffusion distance therefore causes a four-fold increase in the time required for this, a ten-fold increase in the distance causes a hundred-fold increase in the diffusion time, etc. [1]. In other words, diffusion slows down with the distance travelled; the “diffusion front” makes less and less progress per time.

A. Let's take hydrogen chloride as an example: hydrogen chloride has a diffusion constant of $D_{\text{Lit}}^{25°\text{C}} = 0.16\ \text{cm}^2\text{s}^{-1}$ [19]. When diffusing in air, according to equation 11 ($\upsilon = 3$) HCl needs about 1 second to travel 1 cm and 1.6 minutes (100 seconds) to travel 10 cm. To cover *s* = 1 m, 2.7 hours (10,000 seconds) are already required. To spread in a classroom of length *s* = 8 m, HCl would need 7.4 days (640,000 s) by diffusion alone [1,7]. As the example shows, diffusion is only a suitable transport process for *very* short distances – such as at cellular level [1]. Or in other words: Diffusion cannot be responsible for the distribution of substances over long distances within a short time (!), even if perfume (or similar) is typically sprayed in a classroom and its rapid, easily perceptible distribution is sold as diffusion.

But if not diffusion, what is responsible for the odorant’s wide distribution that is in fact observed? The reason for the wide and rapid distribution is the so-called convection, the transport by flow. Convective flows are caused, for one thing, by differences in temperature and the associated differences in density: For example, warm air (lower density) rises upwards, cold air (higher density) sinks downwards which generates a current. Convection can also be forced by movement, e.g. by walking around or even breathing in and out [6,20]. In fact, convection in gases is difficult to avoid: even the mere presence of a single person in a room causes enough convective flow due to their body heat to significantly reduce the influence of diffusion [4]. It is therefore not possible to demonstrate diffusion *alone* in a classroom by spraying perfume (or similar)! This does not mean that diffusion does not also occur: convection is always superimposed on diffusion.

In order to estimate whether diffusion or convection is the dominant transport process over a given distance *L* from the point of origin, the so-called SHERWOOD number (N_{Sh}) can be employed [4]. For the calculation of N_{Sh}, the convection velocity (v_{conv}) is divided by the quotient of the diffusion constant *D* and the considered distance *L* (equation 12). The latter provides the dimension of a velocity, making the SHERWOOD number dimensionless overall [4, 7].

$$N_{Sh} = L \cdot \frac{v_{conv}}{D} \qquad (12)$$

Diffusion only dominates, if $N_{sh}<1$, otherwise convection prevails. With a typical speed of air of not less than 3 cms^{-1} [4], this means for HCl ($D = 0.16\ \text{cm}^2\text{s}^{-1}$), for example, that diffusion is the dominant process only at $L < D/v_{conv} = 0.053$ cm. At $L>0.053$ cm convection already predominates ($N_{Sh}>1$) [7].

B. Dissolving food colouring, ink, etc. in water is also not a diffusion experiment *by the way it is carried out* [4]: It is not uncommon to find instructions to drip a coloured liquid (e.g. a solution of methylene blue) into water in a beaker or similar [4,12]. When the coloured solution is added, it sinks to the bottom quickly [21]. Additionally, clearly visible turbulence forms in the water, whereupon the dye is rapidly distributed in the water [4]. (see Figure 3).

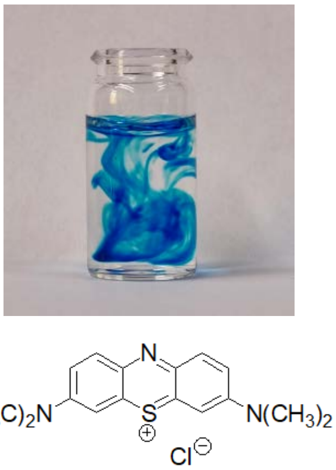

Figure 3. Dripping a solution of methylene blue $C_{16}H_{18}N_3SCl$ (right) into water - clearly *no* diffusion experiment

These dye’s movements observed are often incorrectly referred to as diffusion. However, the sinking of the dye solution is clearly not a diffusion phenomenon, but is due to its higher density compared to water [21]. Furthermore, the turbulence is the unambiguous evidence of a strong convective flow: Corresponding currents are the result of the impact of the droplets on the water. Currents may also already be present in the water, e.g. by movement of the vial used or by filling the water into the vial (*forced convection*). Moreover, diffusion, in which all particles move completely randomly and without direction, cannot produce something as ordered as a vortex (!). In general, beyond any turbulence, the speed of the mixing process is completely incompatible with the process of diffusion [4], which is also 4-5 orders of magnitude slower in liquids than in gases [3]. Taking the diffusion constant of methylene blue ($D = 5 \cdot 10^{-6}$ cm²s^{-1} [4]) into account, it can be easily shown that convection (*not* diffusion) is responsible for the rapid distribution in the experiment described. If we assume, for example, that the snap-cap vial (Figure 3) is filled 3.5 cm high with completely still, flow-free water and a solution of methylene blue is dripped onto the water surface at a speed of v_{conv} =1 cms^{-1}, this results in a Sherwood number of 700,000 (!). The observed mixing of methylene blue that occurs in a short period of time is therefore determined *exclusively* by convection [4]: To overcome a distance of 3.5 cm, methylene blue needed 4.7 days (408,333 s) by diffusion *alone* according to equation 11 ($\upsilon = 3$).

3.2. Genuine Diffusion Experiments

How diffusion can be demonstrated in school classes if superposition with convection in gases and liquids is so difficult to avoid?

A. Only recently school experiments on the diffusion of ammonia [6] and hydrogen chloride [7] were developed which *clearly* show diffusion and which can even be used to determine the diffusion constant D of both gases at school: For this to work, a strip of indicator paper is placed in a glass tube and the glass tube is clamped horizontally. The glass tube is sealed on one side with a stopper. Several cotton swabs are pushed through a single-bored stopper and soaked in at least 6 M ammonia solution or concentrated hydrochloric acid. The stopper prepared in this way is then inserted into the tube from the other side. Hydrogen chloride and ammonia gas are easily set free from their concentrated solutions and spread through the glass tube by diffusion. The diffusion progress of both gases – visible through the blue or red colouring of the indicator paper – can be easily tracked: In both cases, the diffusion starts quickly before slowing down with time or the distance travelled. As expected, HCl (M = 36.5 $gmol^{-1}$) diffuses more slowly than NH_3 (M = 17 $gmol^{-1}$) due to its more than twice as large molecular mass [3,7].

If a sheet of graph paper is placed behind the glass tube, the actual diffusion progress per time can be read off and, if desired, the respective diffusion constants can be quantitatively determined using this data.

Table 2 shows the corresponding diffusion path and diffusion time parameters for approximately the first 30 seconds of each experiment. For more details, please see [6] and [7].

Table 2. path - time parameters for the diffusion of NH_3 and HCl

ammonia NH_3 [6]		hydrogen chloride HCl [7]	
diffusion time t [s]	diffusion path s [cm]	diffusion time t [s]	diffusion path s [cm]
0	0	0	0
4	3	4	2
7	4	8	3
13	5.5	12	3.5
17	6	16	4
23	7	21	4.5

In Figure 4 the path-time values measured for NH_3 and HCl diffusion are plotted in a diagram.

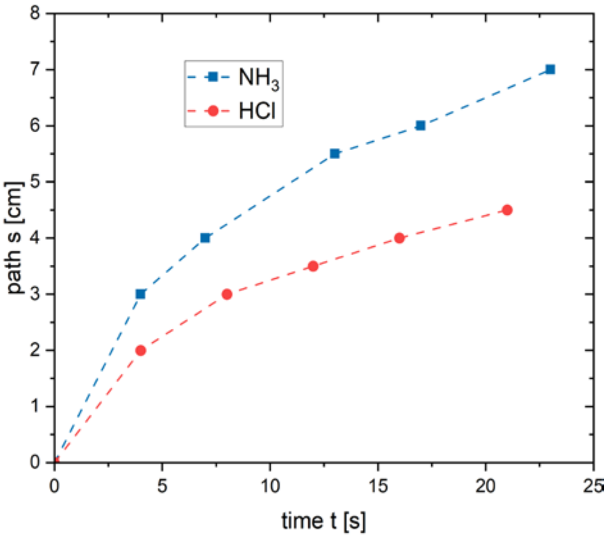

Figure 4. Path - time diagram for the diffusion of NH_3 and HCl

The path-time profiles for HCl and NH_3 in Figure 4 show the deceleration process of diffusion described in section 3.1 graphically: The instantaneous velocity of the macroscopic diffusion process, given by the slope of the tangents in the s(t) diagram, decreases with increasing time (= tangent slope flattens by time). Only at the beginning of the diffusion the spread of the gases is very fast (= large tangent slope). If then the path values (s) are squared (see table 3) and plotted against the diffusion times (t), a straight line going through the origin is obtained in both cases after regression (see Figure 5), i.e. an equation of the type: $s(t)^2 = kt$. This matches exactly the EINSTEIN-SMOLUCHOWSKI equation theoretically derived in section 2.1. [6,7].

Table 3. Path squared-time parameters for the diffusion of NH_3 and HCl

ammonia NH_3 [6]		hydrogen chloride HCl [7]	
diffusion time t [s]	diffusion path squared s² [cm]	diffusion time t [s]	diffusion path squared s² [cm]
0	0	0	0
4	9	4	4
7	16	8	9
13	30.25	12	12.25
17	36	16	16
23	49	21	20.25

Figure 5 shows the diffusion path squared-diffusion time diagram for NH_3 and HCl.

The slope of the two straight lines ($k = 6D$, since $\upsilon=3$, see Eq. 11) results in diffusion constants that are in the range of diffusion constants of gases in air at atmospheric pressure known from literature, e.g. [3, 22]. This clearly identifies both experiments as *genuine* diffusion experiments: For HCl ($k \approx 1.0$ cm²s^{-1}), a diffusion constant of $D = 0.17$ cm²s^{-1} is obtained, which is very close to the literature value ($D_{Lit}^{25°C}$(HCl) = 0.16 cm²s^{-1} [19]). A constant of $D = 0.35$ cm²s^{-1} is calculated for NH_3 ($k \approx 2.1$ cm²s^{-1}) (literature value $D_{Lit}^{25°C}(NH_3) = 0.25$ cm²s^{-1} [23]). With a longer measurement period, a diffusion constant for NH_3 can be obtained that is closer to the actual literature value [6].

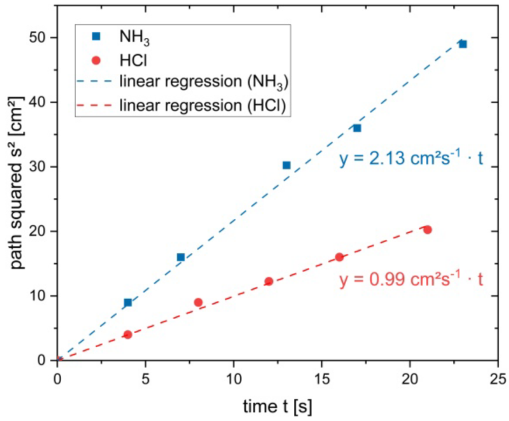

Figure 5. Path² - time diagram for the diffusion of NH_3 and HCl

Convection can be (largely) eliminated in a glass tube as described above. Please note, that however the stopper (provided with the cotton swabs soaked in ammonia solution or hydrochloric acid) should *gently* be placed on the end of the glass tube, as an impulsive and abrupt insertion can also force convection. In general, as mentioned before, convection in gases is very difficult to avoid [4]. This may be the reason why the diffusion constants obtained are higher than the literature values. Yet the experiment allows both *qualitative* statements to be made about the nature of diffusion (range, deceleration over time) and also makes it possible to *quantitatively* extract *reasonable* diffusion constants. The later should only be *optional* in school lessons. However, in the beginners' classes, which also often deal with linear equations in Math at the same time as the introduction of diffusion in Chemistry, a linear equation can be easily determined by students on the basis of Figure 5. Based on the linear relationship $s(t)^2 = kt$ found empirically – a somewhat simplified Einstein -Smoluchowski equation – the characteristics of diffusion can then be discussed in more detail by making simple calculations as shown at the beginning of section 3.1. For more information on the use in teaching please see [7].

B. When dissolving food colouring (or similar) in water, convection can also be avoided by the way the experiment is carried out. In order to generate a *genuine* diffusion experiment, a standing cylinder can be half filled with a coloured solution and then *very carefully* overlaid with water. The initial sharp surface between the coloured solution and the pure water washes out after about a day. According to Heintze [22], the resulting mixing zone increases rapidly at first, but then becomes progressively slower – in accordance with the laws of diffusion (cf. section 3.1). Depending on the dye and the height of the stand cylinder, it can take several weeks to reach complete mixing [22]. Overcoming a distance of 4.25 cm through diffusion alone methylene blue ($D = 5 \cdot 10^{-6}$ cm²s^{-1} [4]) would need (by calculation) almost a whole week.

In theory, the experiment described works well, but in practice it is relatively difficult to implement because not only does evaporation occur over the period of time (the problem could simply be solved by closing the cylinder tightly), but also because layering requires considerable (!) caution and skill [24] in order not to create turbulence, i.e. to avoid convection. It is somewhat easier to add larger crystals of a coloured salt such as copper sulphate to a cylinder filled with water. If the crystals are of sufficient size, they will sink to the bottom without dissolving noticeably and form a saturated solution at the bottom of the cylinder, which then – clearly recognizable – slowly spreads upwards according to the laws of diffusion [25]. Correspondingly large crystals of copper sulphate can be easily obtained when copper sulphate, which is often available as a powder in school, is dissolved in water and the solution is allowed to slowly evaporate: Large crystals form at the bottom of the corresponding container.

However, the exact procedure for setting a sharp interface between a coloured solution and water may look like in detail, there are two other severe problems that come with this kind of experiment: *First*, you have to ensure that the cylinder is protected from vibrations of any kind [24]. Therefore, it is suggested by Conard and Bent [25] to carefully suspend a cylinder with a wire. In my own experience, however, this is also a very delicate operation and easily leads to agitation of the cylinder and therefore convection. *Second*, even if all the steps to avoid any vibration have been successful, due to the slowness of diffusion in liquids, a sample must stand for a long time. Consequently, it is easily exposed to temperature fluctuations (unless the classroom where the experiment is conducted is air-conditioned). Temperature fluctuations, albeit small, can also easily lead to convective flows, not only in gases but also in liquids, which can ruin the diffusion experiment as such [25].

As these considerations show, the demonstration of diffusion *alone* in water over a longer period may be possible in principle, but is difficult to realize in practice. One way of successfully stopping or drastically limiting convection [4] and ensuring that the movement of the solute is exclusively determined by the *random walk* and thus diffusion [26], is to use liquids of very high viscosity. Vogel suggests the use of corn syrup whose viscosity exceeds that of water by a factor of 10^4: Analogously, a dye is dissolved in corn syrup and this mixture is then overlaid with pure corn syrup in a suitable container [4]. Even if convection can be limited in this way, however, it should be considered that the diffusion coefficient and viscosity are inversely proportional to each other [27] and an increase in viscosity therefore also inevitably leads to a reduction in the diffusion coefficient. The spread of the dye is therefore significantly slowed down.

Another, more convenient possibility is the use of gels in which the water is embedded [26], such as those based on gelatine [24], agar-agar [28] or agarose [21]. Usually 1-3% of the gelling agent in water is sufficient to generate corresponding gels [21]. (Water-based) Gels are quite rigid three-dimensional polymer networks whose cavities are filled with a liquid (water). Solutes and solvent can move almost freely in a gel as in the liquid alone, as conductivity measurements show [26]. As a result, the diffusion rates in gels differ only very slightly from the diffusion rates in the pure solvent [28]. The advantage of gels, particularly for schools and students, is that far fewer manual skills are required when setting up a diffusion experiment than when using the solvent alone, as the gels are not significantly affected by movements during transportation, i.e. vibrations etc. [24].

Using various gels in a simple experimental setup, ENDOW and RUSSEL could *qualitatively* compare the different diffusion behaviour of potassium permanganate and methylene blue: They filled a PETRI dish flat with Jello (= brand name for the gelatine used) and drilled a hole in the middle of the gel using a PASTEUR pipette. Then, they added a small volume of an aqueous methylene blue or potassium permanganate solution (c = 100 mM) into the hole whereupon the dissolved dye spreads radially symmetrically by diffusion *alone* (cf. Figure 6) [21]. Since diffusion rates in liquids are a function of the different (STOKES) radii a of the diffusing species ($D \sim 1/a$) [8,27], the potassium permanganate spot increases more than the methylene blue in the same time: The permanganate anion is less bulky than the methylene blue cation and diffuses therefore with a higher rate (please compare with the information given at the end of this section). A clearly visible difference can be seen after 3-4 hours [21].

ENDOW and RUSSEL also used this experimental setup to determine the diffusion constant of methylene blue: The radius of a methylene blue spot (t = 0 s, r_0 = 0.15 cm) increases to approximately $r(t)$ = 0.46 cm within about t = 180 minutes. If the squared radius is plotted against time, a straight line is obtained in accordance with the EINSTEIN-SMOLUCHOWSKI equation. Since methylene blue can only move in the *xy*-plane and thus in the two-dimensional space ($\upsilon = 2$) under the conditions applied, the slope of this straight line corresponds to four times the diffusion constant D (see equation 11). Table 3 shows some of the *rough* time - distance (= radius) parameters obtained by ENDOW and RUSSEL, including the squared radii.

Table 4. Radius - time parameters[3] for the diffusion of methylene blue in Jello, cf [21]

diffusion time t [s]	diffusion radius $r(t)$ [cm]	diffusion radius squared $r(t)^2$ [cm²]
0	0.15	0.023
1,000	0.21	0.044
3,600	0.31	0.096
4,200	0.32	0.10
6,000	0.39	0.15
11,000	0.46	0.21

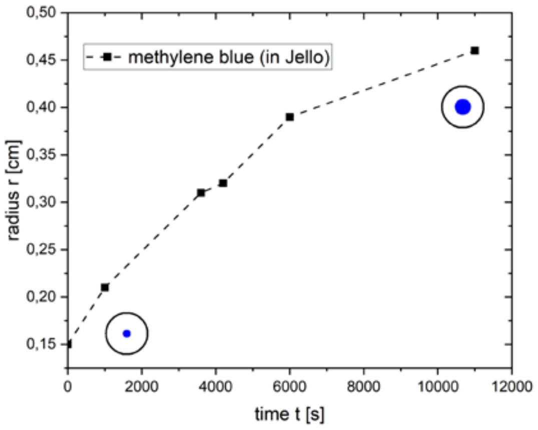

Figure 6. Path (radius) - time diagram for the diffusion of methylene blue in Jello in a petri dish

Figure 6 shows the corresponding diffusion path (radius)-time diagram for the displacement of methylene blue in Jello. In addition, the growth of the initial spot into an increasingly larger one is shown schematically.

The corresponding radius²-time diagram of the diffusion of methylene blue in Jello is shown in Figure 7.

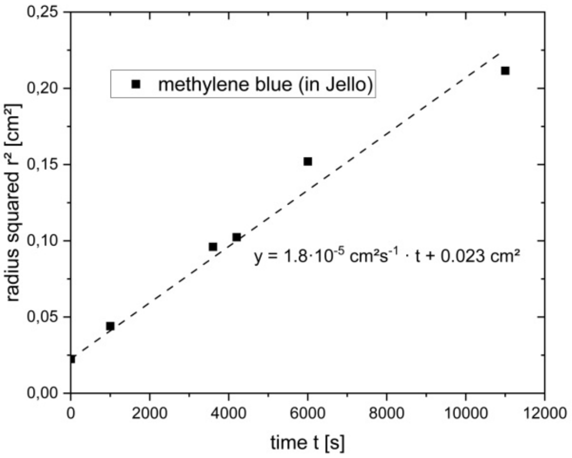

Figure 7. Radius² - time diagram for the diffusion of methylene blue in Jello in a petri dish

In contrast to Figure 5, the graph obtained after linear regression does not go through the origin, since at t = 0 s there is already a spot with an extension of r_0 = 0.15 cm ($r_0^2 \sim 0.023$ cm²). Alternatively, however, $\langle(r(t)-r_0)^2\rangle$ can be calculated and thus the graph can be shifted through the origin according to equation 13 for the two-dimensional diffusion [29]:

$$\langle (r(t)-r_0)^2 \rangle = 4Dt \qquad (13)$$

Whichever representation is chosen, the value $D = (4.5 \cdot 10^{-6})$ cm²s^{-1} [21] is obtained from the slope $k = 4D = (1.8 \cdot 10^{-5})$ cm²s^{-1} in agreement with the literature value of the diffusion constant of methylene blue in water ($D = 5 \cdot 10^{-6}$ cm²s^{-1} [4]). The magnitude of the diffusion constant obtained clearly indicates that the experiment is a *genuine* diffusion experiment.

At this point, it should not be concealed that the first genuine diffusion experiment described in this article, i.e. the diffusion of HCl, NH_3 into air (at atmospheric pressure in a sealed tube) is concentration-*in*dependent, whereas in the case of solutes like methylene blue in water, diffusion and thus the diffusion constant are concentration-dependant [30]: In ideal gases, the gas particles are separated by such a large distance that they do not affect each other. In aqueous solutions, on the other hand, the distance between the dissolved particles is a function of the concentration and an increase in concentration causes the dissolved particles to come closer and closer together. At high solute concentration, the close proximity of the ions finally results in additional interactions [8]: In the case of electrolytes higher ion aggregates are often formed [27,31]. Associated species have a larger volume than the single diffusing species and thus diffuse in solution at a lower rate [27]. For example, when investigating the diffusion behaviour of copper chloride in aqueous solution at different concentrations, RIBEIRO et al. found that the diffusion constant decreases with increasing concentration, which was interpreted as a result of aggregates of the type

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[3] ENDOW and RUSSEL have not provided the raw data. Instead, the values were read from the diagram on page 7 of [21] as best as possible.

$Cu_{1+n}(OH)_{2n}^{2+}$ formed by the hydrolysis and complexation of the salt studied [31].

In practice, diffusion measurements in liquids are carried out at different concentrations of the solutes. The diffusion constant is then calculated by extrapolating the experimental data to $c \rightarrow 0$ M [30,31]: At infinite dilution, the ions are so far apart that they can no longer interact with each other, like particles in ideal gases [8]. Please note, that however, anions and cations cannot exist on their own: For reasons of electroneutrality, anions must always be kept in the vicinity of cations and *vice versa* [32]. Even in infinitely diluted solutions of a strong electrolyte, in which the completely dissociated ions no longer interact with each other, the electroneutrality condition prevents macroscopic charge separation from occurring. *Without* an external electric field, which is known to be able to separate ions according to their charge, "*anions and cations diffuse through the solvent effectively as a single component (salt), similarly to the molecular diffusion of neutral species, and not like single ionic species*" [33, p. 3–4]. Consequently, the diffusion process of an electrolyte depends on the diffusion constant of both the cation and anion and the diffusion as such is designated by the diffusion constant D_{salt} ($D_{\pm}$) which is referred to as *ambipolar* ("*salt*") *diffusion constant* [33] or *mutual diffusion constant* [34].

Consider for example the electrolyte solution of a binary salt ($A_{\nu+}B_{\nu-}$) with ν_+A^{z+} cations and ν_-B^{z-} anions, where ν_i indicates the stoichiometry coefficient and z_i the charge of the respective ionic species i. If D_i^0 denotes the diffusion coefficient of the *individual* ionic species i at infinite dilution ($c \rightarrow 0$ M), where + indicates the cation and – the anion, the (mutual) diffusion constant of the salt ($D_{\pm}$) can be calculated using equation 14 [33,34].

$$D_{\pm}^0 = \frac{D_+^0 \cdot D_-^0 \cdot (\nu_+ + \nu_-)}{\nu_- \cdot D_+^0 + \nu_+ \cdot D_-^0} \qquad (14)$$

Equation 14 shows that the diffusion constant of a salt is composed of the diffusion constants of its components. However, if in general the cation (anion) diffuses much more slowly than the anion (cation) due to its larger size, the diffusion current is mainly determined by the cation (anion) (cf. [35]), as can also be seen from equation 14. This, for example, applies to the diffusion of methylene blue (see Figure 3) in water or water-based gels: The cation $C_{16}H_{18}N_3S^+$, not the much smaller chloride anion (Cl^-), governs the diffusion flux of the dye.

4. Conclusion

Diffusion is a frequently misunderstood and incorrectly taught transport process that is not rarely held responsible for all forms of particle distribution in everyday life, even though convection, a flow phenomenon, and *not* diffusion, is the dominant process over long distances.

Diffusion is only extremely efficient over *very* short distances. It is driven by the maximization of the entropy of mixing, whereby a matter-related inhomogeneity in a closed system leads to a concentration equalization through the random, undirected movement of the particles. The random particles' movement (the so-called *random walk*) makes it possible to establish a relationship between diffusion time t and diffusion path s, the EINSTEIN-SMOLUCHOWSKI equation, by using simple probability calculations. The EINSTEIN -SMOLUCHOWSKI equation ($s^2 = \upsilon \cdot 2Dt$, υ represents the spatial dimension) identifies diffusion clearly as an effective short-distance transport process and illustrates that the *macroscopically* observable diffusion decelerates rapidly over time, which accordingly can be observed in *correctly* conducted diffusion experiments.

Convection, on the other hand, is forced by motion or caused by temperature or density differences and is responsible for the rapid distribution of colorants dripped into a glass of water or for the rapid distribution of odorants released into a room. Both experiments should therefore be banned for demonstrating diffusion, as they unequivocally show convection. It is recommended to replace them by the experiments characterized in this article as *genuine* diffusion experiments, i.e. the "distribution of HCl or NH_3 in a glass tube" and the "distribution of methylene blue in water-based gels". In the latter case, gels can replace water since solutes can move almost as freely in a gel as in water, so that the diffusion rates in both cases differ only slightly from each other.

In all diffusion experiments that have been suggested in this article convection can be restricted sufficiently well. In addition, these experiments allow diffusion constants to be determined quantitatively at school (if wanted) with help of the EINSTEIN-SMOLUCHOWSKI equation. This ultimately identifies them as *genuine diffusion experiments* alongside the pure macroscopic observations than can be made and that agree with the laws of the nature of diffusion.

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