ANALYTICAL SOLUTIONS FOR FIRST ORDER SORPTIVE UPTAKE OR DESORPTION KINETICS

1. EQUILIBRATION TIME PERIODS IN FILM DIFFUSION CONTROLLED MASS TRANSFER

The simplest case for sorption or desorption kinetics (and which often is not the appropriate model) is diffusion of a solute through a stagnant boundary layer, i.e. a water film, as shown in Fig. 1 with concentration gradients for the desorption case for the finite and infinite bath boundary condition. The finite bath is the most common case in the lab since sorption/desorption kinetics are conducted in bottles (vials) with a finite volume of water. Infinite bath conditions may be encountered during remediation, e.g. when contaminated particles are permanently purged with clean water keeping the concentration outside of the particles close to zero (as if they were in an infinitely large volume of clean water).

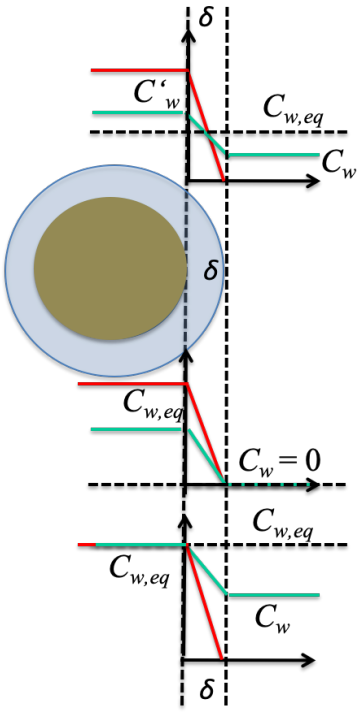


Fig. 1.1: Aqueous concentrations (C_w) for film diffusion (δ: film thickness) during desorption – red and green gradients are initial and intermediate concentrations, horizontal dashed lines denote final or equilibrium concentration ($C_{w,eq}$); top: finite bath - loss of solute from the solid phase resulting in increasing aqueous concentrations until equilibrium is reached; middle: infinite bath - concentration in water is always zero (infinite amount of water); bottom: strong sorption - stable concentrations at the solid/water interface e.g. during mineral dissolution (no or relatively little solute mass is desorbed or dissolved and goes into the aqueous phase until equilibration) or small amounts of water (low liquid-to-solid ratio). The flux density through the aqueous boundary layer is given by Fick's 1st law: $F = - D_{aq}/\delta\ (C'_w - C_w)$

In order to illustrate the interplay of the different parameters (specific surface area, grain size, distribution coefficients) in the following the analytical solutions for film diffusion limited transfer kinetics are derived (also called "first order"). Initially all the solute is either associated with the particles (desorption) or in the water (sorption). If a certain mass of solids is in contact with a limited volume of water (e.g. laboratory batch experiments with bottles or during pre-equilibration in a column test) the approach to equilibrium of a solute (initially in the water or associated/sorbed to the solids) depends on the mass of sorbent or solids (m_d) and the volume of water (V_w) in the system. The mass balance in such a system expressed by the respective rates is:

$$V_w \frac{\partial C_w}{\partial t} = - m_d \frac{\partial C_s}{\partial t} \tag{1.1}$$

Thus, the mass gained (or lost) in the water equals the mass lost (or gained) from the solids. If we introduce the liquid solid ratio LS (= V_w/m_d) we get:

$$LS \frac{\partial C_w}{\partial t} = - \frac{\partial C_s}{\partial t} \tag{1.2}$$

After a certain time, equilibrium between concentrations in the solids and water will be obtained:

$$C_{s,eq} = K_d \, C_{w,eq} \tag{1.3}$$

where K_d denotes the distribution coefficient [l kg^{-1}]. K_d/LS (= $K_d \, m_d/V_w$) denotes the ratio of the mass sorbed to the particles ($M_{s,eq}$) to the mass of solute in water ($M_{w,eq}$) under equilibrium conditions (= $M_{s,eq}/M_{w,eq} = C_{w,eq} \, K_d \, m_d \, / \, C_{w,eq} \, V_w = K_d \, m_d \, / \, V_w$). If we assume uniform concentrations inside the particles and completely mixed conditions in aqueous phase separated by an external mass transfer resistance (i.e. diffusion in the water film surrounding each particle) then mass transfer follows Fick's first law:

$$\begin{aligned} F &= \frac{D_{aq}}{\delta} \frac{3 \, m_d}{r \, \rho} (C'_w - C_w) = k \, A \, (C'_w - C_w) \\ \frac{F}{V_w} &= \frac{\partial C_w}{\partial t} = \frac{D_{aq}}{\delta} \frac{3 \, m_d}{r \, \rho \, V_w} (C'_w - C_w) = k \, A^o (C'_w - C_w) \end{aligned} \tag{1.4}$$

r, ρ and δ denote radius and bulk density of the particle and the film thickness for mass transfer, respectively. the term $m_d \, 3/(\rho \, r)$ denotes the total surface area available for diffusion (i.e. the solids volume = m_d/ρ divided by the volume of one sphere = $4/3 \, \pi \, r^3$ (= number of spheres) times the surface are of one sphere = $4 \, \pi \, r^2$). Normalization of the flux F to a finite volume of water V_w leads to the change of concentration ($\partial C_w/\partial t$); k (= D_{aq}/δ) and A^o (= $m_d \, 3/(\, V_w \, \rho \, r)$) are the mass transfer coefficient [m s^{-1}] and the specific surface area per unit volume of water [m^2 m^{-3} = m^{-1}]. Note, the term $3/(\rho \, r)$ denotes the specific surface area per dry mass of the particles e.g. in m^2 g^{-1}. C'_w is the unknown concentration at the particle/water interface where local equilibrium conditions apply ($C'_w = C_s/K_d$); C_w is the concentration in bulk water at a given time.

Eq. 1.4 may be easily solved depending on the boundary conditions. We distinguish two cases: the **finite bath**, i.e. particles suspended in a limited volume of water (e.g. in a bottle in the lab), and the **infinite bath** where particles are in infinite volume of water (e.g. in the ocean). Generally, infinite bath boundary conditions are easier to solve because C'_w is known and fixed.

Infinite bath boundary conditions. Imagine a particle loaded arrives in the ocean (or a clean particle arrives in the ocean and takes up a solute from the water). For desorption in the infinite bath C_w is fixed (= 0) it makes sense to monitor C_s. Note, the concentration difference is positive and this results in a negative flux (the particles are losing) and thus we get C_w = 0 and $C'_w = C_s/K_d$:

$$\frac{\partial C_s}{\partial t} = - \frac{D_{aq}}{\delta} \frac{3}{\rho \, r} (C'_w - 0) = -k \frac{3}{\rho \, r} \left(\frac{C_s}{K_d} - 0 \right) = - \frac{k}{K_d} \frac{3}{\rho \, r} C_s \tag{1.5}$$

Upon integration Eq. 1.5 yields the following analytical solutions for desorption and sorption:

$$\int_{C_{s,o}}^{C_s} \frac{\partial C_s}{C_s} = \int_0^t - \frac{k}{K_d} \frac{3}{\rho \, r} \partial t \tag{1.6}$$

$$\ln(C_s) - \ln(C_{s,o}) = \ln\left(\frac{C_s}{C_{s,o}}\right) = -\frac{k}{K_d}\frac{3}{\rho\, r}t$$

$$\frac{C_s}{C_{s,o}} = \exp\left(-\frac{k}{K_d}\frac{3}{\rho\, r}t\right)$$

for sorption $C_{w,eq}$ would be fixed (other way around):

$$\frac{\partial C_s}{\partial t} = -\frac{D_{aq}}{\delta}\frac{3}{\rho\, r}\left(C_w' - C_{w,eq}\right) = -k\frac{3}{\rho\, r}\left(\frac{C_s}{K_d} - \frac{C_{s,eq}}{K_d}\right) = -\frac{k}{K_d}\frac{3}{\rho\, r}\left(C_s - C_{s,eq}\right)$$

$$\int_0^{C_s} \frac{\partial C_s}{C_s - C_{s,eq}} = \int_0^t -\frac{k}{K_d}\frac{3}{\rho\, r}\,\partial t$$

$$\ln\left(C_s - C_{s,eq}\right) - \ln\left(0 - C_{s,eq}\right) = \ln\left(-\frac{C_s}{C_{s,eq}} + 1\right) = -\frac{k}{K_d}\frac{3}{\rho\, r}t$$

$$\frac{C_s}{C_{s,eq}} = 1 - \exp\left(-\frac{k}{K_d}\frac{3}{\rho\, r}t\right)$$

=> for film diffusion in the infinite bath, desorption/sorption time scales increase with increasing K_d

Finite bath (batch system). In a limited volume of water (in a "bottle") the unknown concentration at the interface C'_w in eq. 1.4 can be calculated assuming mass conservation in the system. C'_w is in equilibrium with the concentration in the solids, C_s, which is obtained from the total mass in the system (for desorption = initial mass in the solids $C_{s,o}\ m_d$; for sorption = initial mass in the water $C_{w,o}\ V_w$) minus the actual mass in the water $C_w\ V_w$. Note, under equilibrium conditions the total mass in the system is given by the sum present in the water and the solids ($C_{s,eq}\ m_d + C_{w,eq}\ V_w$), following mass conservation:

$$C_w' = \frac{C_s}{K_d} = \frac{C_{s,eq}\ m_d + C_{w,eq}V_w - C_wV_w}{K_d\ m_d} =$$
$$C_{w,eq} + \frac{C_{w,eq}V_w}{K_d\ m_d} - \frac{C_wV_w}{K_d\ m_d} = C_{w,eq}\left(1 + \frac{V_w}{K_d\ m_d}\right) - \frac{C_wV_w}{K_d\ m_d} \qquad (1.7)$$

The concentration difference then is:

$$C_w' - C_w = C_{w,eq}\left(1 + \frac{V_w}{K_d\ m_d}\right) - \frac{C_wV_w}{K_d\ m_d} - C_w = \left(1 + \frac{V_w}{K_d\ m_d}\right)\left(C_{w,eq} - C_w\right) \qquad (1.8)$$

Thus eq. 1.4 becomes:

$$\frac{\partial C_w}{\partial t} = k\ A^o\left(1 + \frac{V_w}{K_d\ m_d}\right)\left(C_{w,eq} - C_w\right) \qquad (1.9)$$

which upon integration yields the following analytical solution for the initial condition $C_{w(t=0)} = 0$ (desorption):

$$\int_0^{C_w} \frac{\partial C_w}{C_{w,eq} - C_w} = \int_0^t k\ A^o\left(1 + \frac{V_w}{K_d\ m_d}\right)\partial t \qquad (1.10)$$

$$-\ln\left(C_{w,eq} - C_w\right) + \ln\left(C_{w,eq}\right) = -\ln\left(1 - \frac{C_w}{C_{w,eq}}\right) = k\, A^o \left(\frac{V_w}{K_d\, m_d} + 1\right) t$$

$$\frac{C_w}{C_{w,eq}} = 1 - \exp\left(-k\, A^o \left(1 + \frac{V_w}{K_d\, m_d}\right) t\right)$$

$$\text{with } A° = \frac{m_d\, 3}{\rho\, r\, V_w}$$

$$\frac{C_w}{C_{w,eq}} = 1 - \exp\left(-\frac{k}{K_d}\frac{3}{\rho\, r}\left(1 + K_d\, \frac{m_d}{V_w}\right) t\right)$$

Since V_w is constant, C_w and $C_{w,eq}$ equal the mass which has diffused out of the sphere after some time and after equilibrium was reached:

$$\frac{M}{M_{eq}} = 1 - \exp\left(-\frac{k}{K_d}\frac{3}{\rho\, r}\left(1 + K_d\, \frac{m_d}{V_w}\right) t\right)$$

The advantage of the notation M/M_{eq} is that it is independent on the direction (sorptive uptake or desorption) and thus we will stick to that in the following. For sorptive uptake it corresponds to the relative concentration in the solids. In batch experiments often the concentration in water is monitored (see Box 1 for relative changes in concentrations in water). Note for small m_d/V_w infinite batch conditions are reached again and eq. 1.10 reduces to eq. 1.6. The rate constant in Eq. 1.10 (everything in the argument of the exponential function before the time) is almost the same as in in eq. 1.6 but now we have in addition the term $1 + K_d\, \frac{m_d}{V_w}$ which just denotes the ratio of total solute mass in the system ("capacity") to the fraction in water (note, this corresponds to the retardation factor in a porous media (= $1 + K_d\, \frac{\rho_b}{n}$; ρ_b and n then denote the dry bulk density and the porosity)). For small solid to water ratios (m_d/V_w) and/or small K_d values the rate constant in eq. 1.10 is the same as in the infinite bath (eq. 1.6). For large solid to water volumes (m_d/V_w) and/or large K_d values the rate constant becomes independent on K_d. The invers of the rate constant is a characteristic time which is shown as a function of K_d and LS in Fig 2.2.

=> in sorption/desorption in the finite bath ("bottle") film diffusion time scales become independent on K_d if K_d values exceed LS and increase with increasing water to solids ratios

Box 1. Aqueous concentrations in a batch system (bottle)

If we want to follow the decrease in aqueous concentrations during sorptive uptake experiments (which is a frequent case) and following solution is obtained for the initial $C_{w(t=0)} = C_{w,0}$:

$$\int_{C_{w,0}}^{C_w} \frac{\partial C_w}{C_{w,eq} - C_w} = \int_0^t k\, A^o \left(1 + \frac{V_w}{K_d\, m_d}\right) \partial t$$

$$-\ln\left(C_{w,eq} - C_w\right) + \ln\left(C_{w,eq} - C_{w,0}\right) = k\, A^o \left(1 + \frac{V_w}{K_d\, m_d}\right) t$$

$$\frac{C_{w,eq} - C_w}{C_{w,eq} - C_{w,0}} = \exp\left(-k\, A^o \left(1 + \frac{V_w}{K_d\, m_d}\right) t\right)$$

and with $A° = \frac{m_d\, 3}{\rho\, r\, V_w}$

$$C_w = C_{w,eq} - \exp\left(-\frac{k}{K_d}\frac{3}{\rho\, r}\left(1 + K_d\frac{m_d}{V_w}\right) t\right)\left(C_{w,eq} - C_{w,0}\right)$$

normalization to $C_{w,eq}$ leads to

$$\frac{C_w}{C_{w,eq}} = 1 + \mathrm{K_d}\frac{m_d}{V_w}\exp\left(-\frac{k}{K_d}\frac{3}{\rho\, r}\left(1 + K_d\frac{m_d}{V_w}\right) t\right)$$

and normalization to $C_{w,o}$ yields

$$\frac{C_w}{C_{w,o}} = \frac{1}{1 + K_d\frac{m_d}{V_w}}\left(1 + K_d\frac{m_d}{V_w}\exp\left(-\frac{k}{K_d}\frac{3}{\rho\, r}\left(1 + K_d\frac{m_d}{V_w}\right) t\right)\right)$$

For large water volumes, we obtain again the infinite bath solution and kinetics slow down. For large K_d (or m_d/V_w), K_d drops out and the change in aqueous becomes independent on sorption capacity of the solids; this applies if $C_{w,eq}$ is less than 0.1 of $C_{w,0}$ – which may be considered in sorption kinetic experiments ($C_{w,eq}$ then may be neglected and we get eq. 1.12). For t =0, $C_w/C_{w,eq}$ denotes the total to the dissolved mass (= 1+$K_d\, m_d/V_w$) and $C_w/C_{w,o}$ = 1. For $t = \infty$ $C_w/C_{w,eq}$ becomes 1 and and $C_w/C_{w,o}$ = 1 denotes the the fraction dissolved (= 1/(1+$K_d\, m_d/V_w$)).

Box 2. "Apparent" K_d

Often relative distribution coefficients are used to illustrate sorption kinetics in batch experiments. This has the advantage that sorptive uptake data become independent on the solid to liquid ratio at least at early time. Relative distribution coefficients are defined as the ratio of the apparent distribution coefficient $K_{d,a}$ to the equilibrium K_d (= $K_{d,a}/K_d$). We start with eq. 10b (note that concentration differences were changed by multiplication by -1 in numerator and denominator):

$$\frac{C_w - C_{w,eq}}{C_{w,0} - C_{w,eq}} = \exp\left(-\frac{k}{K_d}\frac{3}{\rho\, r}\left(1 + K_d\frac{m_d}{V_w}\right)t\right)$$

realizing that $(C_{w,0} - C_{w,eq})V_w$ represents the mass sorbed under equilibrium condition ($C_{s,eq}\, m_d$) and ($C_w - C_{w,eq}$)V_w (the mass in the water to be sorbed) equals ($C_{s,eq} - C_s$)m_d leads to the relative change of the concentration in the solids:

$$\frac{C_s}{C_{s,eq}} = 1 - \exp\left(-\frac{k}{K_d}\frac{3}{\rho\, r}\left(1 + K_d\frac{m_d}{V_w}\right)t\right)$$

Extending that to relative K_d's:

$$\frac{C_s\, C_{w,eq}}{C_{s,eq}\, C_w} = \frac{K_{d,a}}{K_d} = \frac{1 - \exp\left(-\frac{k}{K_d}\frac{3}{\rho\, r}\left(1 + K_d\frac{m_d}{V_w}\right)t\right)}{\frac{C_w}{C_{w,eq}}}$$

C_w is known from eq. 1.10b and we get:

$$\frac{K_{d,a}}{K_d} = \frac{1 - \exp\left(-\frac{k}{K_d}\frac{3}{\rho\, r}\left(1 + K_d\frac{m_d}{V_w}\right)t\right)}{1 - \exp\left(-\frac{k}{K_d}\frac{3}{\rho\, r}\left(1 + K_d\frac{m_d}{V_w}\right)t\right)\left(1 - \frac{C_{w,0}}{C_{w,eq}}\right)}$$

For short time periods, we may replace the numerator by the negative argument of the exponential function ($1\text{-}e^{-x} \approx x$) and realizing that the exponential function in the denominator approaches unity at early times we get a short term approximation:

$$\frac{K_{d,a}}{K_d} \approx \frac{\frac{k}{K_d}\frac{3}{\rho\, r}\left(1 + K_d\frac{m_d}{V_w}\right)t}{1 - \left(1 - \frac{C_{w,0}}{C_{w,eq}}\right)} = \frac{\frac{k}{K_d}\frac{3}{\rho\, r}\left(1 + K_d\frac{m_d}{V_w}\right)t}{\frac{C_{w,0}}{C_{w,eq}}}$$

$C_{w,0}$ represents the total mass in the system ($C_{w,eq}\, V_w + C_{s,eq}\, m_d$) divided by V_w:

$$\frac{K_{d,a}}{K_d} \approx \frac{\frac{k}{K_d}\frac{3}{\rho\, r}\left(1 + K_d\frac{m_d}{V_w}\right)t}{\frac{C_{w,eq}V_w + C_{s,eq}m_d}{C_{w,eq}V_w}} = \frac{\frac{k}{K_d}\frac{3}{\rho\, r}\left(1 + K_d\frac{m_d}{V_w}\right)t}{1 + \frac{C_{s,eq}m_d}{C_{w,eq}V_w}} = \frac{\frac{k}{K_d}\frac{3}{\rho\, r}\left(1 + K_d\frac{m_d}{V_w}\right)t}{1 + K_d\frac{m_d}{V_w}} = \frac{k}{K_d}\frac{3}{\rho\, r}t$$

Therefore at early times $K_{d,a}/K_d$ is independent on the solids to liquid ratio (m_d/V_w).

...thus $K_{d,a}$ is also independent on K_d at early times and could explain many observations on accumulation of strongly hydrophobic compounds on organic particles in air or biota in lakes which e.g. lack a clear correlation to K_{ow} of the compounds (e.g. B. Barbas et al. 2018: Gas/particle partitioning and particle size distribution of PCDD/Fs and PCBs in urban ambient air. Science of The Total Environment, https://doi.org/10.1016/j.scitotenv.2017.12.114).)

This result may also be obtained from the early time approximation of eq. 1.6:

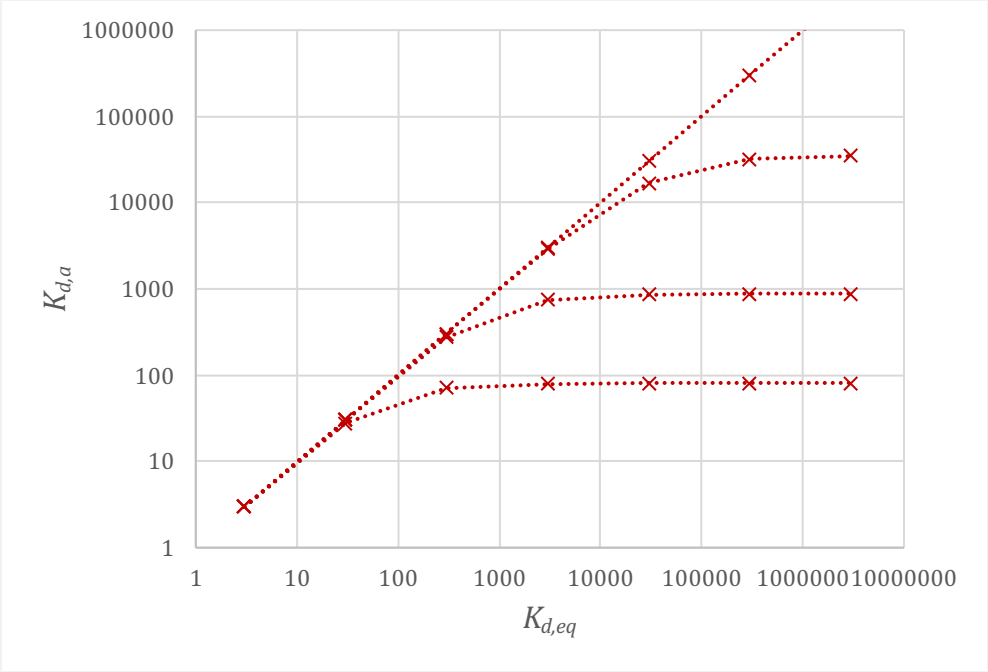
$$\frac{C_s}{C_{s,eq}} = \frac{k}{K_d}\frac{3}{\rho\, r}t$$

using $C_{s,eq} = C_{w,eq}\, K_d$:

$$C_s = \frac{k}{K_d}\frac{3}{\rho\, r}\, t\, C_{w,eq}\, K_d = k\frac{3}{\rho\, r}\, t\, C_{w,eq}$$

Thus, sorptive uptake at early times is independent on K_d (and thus the compound), which for instance is relevant for passive sampler design (see chap. 5). Initially the sorbent acts as infinite sink for all compounds. Finally, this leads to the apparent $K_{d,a}$:

$$K_{d.a} = \frac{C_s}{C_{w,eq}} = k\frac{3}{\rho\, r}t$$



$K_{d,apparent}$ vs. K_d at equilibrium after 1, 9, 53 and 213 days (from bottom to top) in a batch sorptive uptake mode; grain size = 2 mm, Sherwood number =2 (low Reynolds numbers), $D_{aq} = 7 \times 10^{-10}$ m^2 s^{-1} ; LS = 1000 : 1 l kg^{-1} ; similar plots would be obtained if we plot $K_{d,apparent}$ vs. K_{ow}, K_{oc} or S.

"Infinite" sorption (the sorbent takes or keeps it all). If in the finite bath a large fraction (e.g., > 90%) is sorbed (uptake mode) or insignificant desorption during release occurs (infinite sorption), then C_w' is either zero all the time or corresponds to the final equilibrium desorption ($C_{w,eq}$); in this case $K_d\, m_d/V_w$ becomes very big and K_d drops out in eq. 1.10:

$$\frac{M_w}{M_{w,eq}} = 1 - \exp\left(-k\frac{3}{\rho\, r}\frac{m_d}{V_w}t\right) \qquad (1.11)$$

In this case rates are independent on K_d. Relative concentrations in water then are, e.g.:

for desorption (1.12)

$$\frac{C_w}{C_{w,eq}} = 1 - \exp\left(-k\frac{3}{\rho\, r}\frac{m_d}{V_w}t\right)$$

And for sorptive uptake

$$\frac{C_w}{C_{w,o}} = \exp\left(-k\frac{3}{\rho\, r}\frac{m_d}{V_w}t\right)$$

The desorption case describes the concentration increase in the finite bath for dissolution of minerals with a constant concentration at the surface. Note similarities to eq. 1.6 if in eq. 1.10 the liquid solid ratio (V_w/m_d) goes to infinity.

=> for large sorption capacities and/or large solid/water ratio sorption/desorption time scales for film diffusion are independent of K_d

In general sorption/desorption kinetics especially in batch systems depend on boundary conditions (and differ for film diffusion, intraparticle diffusion and intraparticle pore diffusion, see next chapter) as summarized here:

$$\frac{M}{M_{eq}} = 1 - \exp\left(-\frac{k}{K_d}\frac{3}{\rho\, r}\left(1 + K_d\frac{m_d}{V_w}\right)t\right)$$

In the infinite bath (V_w ➔ infinity), the term in parenthesis drops out:

$$\frac{M}{M_{eq}} = 1 - \exp\left(-\frac{k}{K_d}\frac{3}{\rho\, r}t\right)$$

and time scales increase with increasing K_d.

For strong sorption in the finite bath (almost everything sorbs during sorptive uptake or only little mass is released in desorption (non-depletive)), K_d drops out and is "replaced" by V_w/m_d:

$$\frac{M}{M_{eq}} = 1 - \exp\left(-k\frac{3}{\rho\, r}\frac{m_d}{V_w}t\right)$$

… time scales now increase with V_w/m_d. Strong sorption or non-depletive desorption is often encountered in sorption batch experiments and leaching tests.

Note, this applies for a homogeneous sample, if only a fraction of the solids (e.g., just the particulate organic matter) participates in sorption desorption, then m_d decreases and time scales become much longer (the volume of the reactive particles and thus their surface area is now much smaller and thus mass transfer is slower).

Box 3: The fraction dissolved and finite vs. infinite bath conditions

In a batch experiment the fraction of dissolved compound decreases with increasing sorption coefficients and this also marks the transition from infinite to finite bath boundary conditions for sorption/desorption kinetics.

The fraction dissolved is:

$$f_{diss} = \frac{C_w\, V_w}{C_w\, V_w + C_s\, m_d} = \frac{1}{1 + \frac{C_s\, m_d}{C_w\, V_w}} = \frac{1}{1 + K_d \frac{m_d}{V_w}}$$

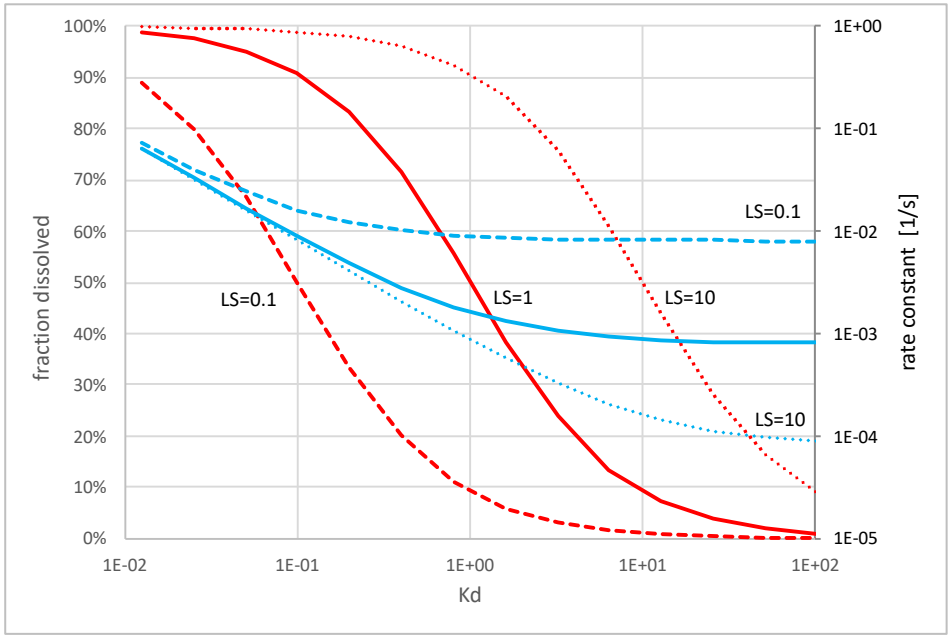
If K_d equals the liquid to solid ratio ($LS = V_w/m_d$), the denominator becomes 2 and 50% are dissolved and 50% sorbed. For K_d 10 times larger than LS only about 9% are dissolved (for K_d 10 times smaller than LS 90% are already dissolved).

Generally, the rate constant in a batch system is (see eq. 1.10):

$$\lambda = \frac{k}{K_d} \frac{3}{\rho\, r} \left(1 + K_d \frac{m_d}{V_w}\right)$$

If K_d becomes much smaller than LS, then the term in parenthesis becomes 1 and the rate constant decreases with increasing K_d (infinite bath). If K_d becomes much larger than LS, then the rate constant becomes independent on K_d and this marks the transition from the infinite to the finite bath boundary conditions. The rate constant then is higher than under infinite bath conditions and increases with decreasing LS, which corresponds to an increasing specific surface area:

$$= \frac{m_d\, 3}{V_w\, \rho\, r}$$



2. CHARACTERISTIC TIMES

2.1 HOMOGENOUS SYSTEMS

If the argument of the exponential function in eq. 1.10 equals -1 we get 1 - exp(-1) = 0.6321 and 63.2% of M/M_{eq} (or any relative concentration) are reached. Thus, a simple characteristic time after that equilibrium is achieved to 63.2% can be defined:

$$t_{0.63} = \frac{1}{k\,A^o\left(1+\frac{V_w}{K_d\,m_d}\right)} = \frac{1}{k\,\frac{3\,m_d}{\rho\,r\,V_w}\left(1+\frac{V_w}{K_d\,m_d}\right)} = \frac{1}{k\,\frac{3}{\rho\,r}\left(\frac{m_d}{V_w}+\frac{1}{K_d}\right)} = \frac{1}{\frac{D_{aq}}{\delta}\frac{3}{\rho\,r\,K_d}\left(1+K_d\frac{m_d}{V_w}\right)} \quad (2.1)$$

The denominator corresponds to the first order rate constant – the inverse is the characteristic time. In the infinite bath, the solids to liquid ratio (m_d/V$_w$) goes to zero and the characteristic time becomes:

$$t_{0.63} = \frac{1}{\frac{D_{aq}}{\delta}\frac{3}{r\,\rho\,K_d}} \quad (2.2)$$

For 90% and 99% equilibration it takes 2.3 and 4.6 times longer than for 63%. Eqs. 2.1 and 2.2 differ by the factor 1 + $K_d\,m_d/V_w$ illustrating that t_{ch} in the infinite bath is retarded compared to the finite bath (the former takes 1 + $K_d\,m_d/V_w$ times longer).

If K_d and/or m_d/V_w get large (infinite sorbent – finite bath), then K_d drops out (and is quasi replaced by V_w/m_d).

$$t_{0.63} = \frac{1}{\frac{D_{aq}}{\delta}\frac{3}{r\,\rho}\frac{m_d}{V_w}} \quad (2.3)$$

While in the finite bath the characteristic time t_{ch} becomes independent on K_d (if $K_d >> V_w/m_d$) in the infinite bath t_{ch} always increases with increasing K_d. The term $K_d\,m_d/V_w$ denotes the ratio of the mass sorbed to the solids and the mass in solution after equilibrium, which in a typical sorptive uptake batch experiment should be larger than one in order to keep errors in the mass balance calculation reasonably low (the initial aqueous concentration after spiking drops by 50 % until equilibrium is reached). Therefore, characteristic times in batch experiments often follow eq. 2.3 and tend to be independent on K_d.

In consequence, t_{ch} may be vastly different depending on boundary conditions (infinite bath *vs.* infinite sorbent); the ratio of the infinite bath and finite bath characteristic times (eq. 2.2 / eq. 2.3) then equals: $K_d\,m_d/V_w$.

2.2 HETEROGENEOUS SYSTEMS – PARTICLE MIXTURES

In heterogeneous systems (i.e. mixtures of particles with different properties such as size or sorption capacity) kinetics may get quite complicated as different particle classes may compete with each other for the solute and thus different boundary conditions may be experienced (finite vs. infinite bath). A simple example for assessing characteristic times can consist of a mixture of

slowly sorbing coarse particles with fine particles which are always at equilibrium with water; for that in eq. 2.1 the water volume (V_w) has also to account for the mass in the fine particles:

$$t_{0.63} = \frac{1}{\frac{D_{aq}}{\delta}\frac{3}{\rho\, r_{coarse}\, K_{d,coarse}}\left(1 + K_{d,coarse}\frac{m_{coarse}}{V_w + K_{d,fine}\, m_{fine}}\right)} \tag{2.4}$$

For the sake of simplicity, we may assume the same K_d for fine and coarse particles. If now $K_d\, m_{fine}$ gets larger than V_w, then K_d in the parenthesis drops out and if furthermore m_{coarse}/m_{fine} is smaller than one (which likely is the case), then the coarse particles experience infinite bath conditions (eq. 2.2) and thus t_{ch} for them becomes much bigger depending on K_d. Equilibration of the coarse particles is now (if the second term in parenthesis is bigger than 1) retarded by the factor (V_w + $K_{d,fine}\, m_{fine}$)/V_w = 1 + $K_{d,fine}\, m_{fine}/V_w$ compared to water alone.

If we assume, that fine particles equilibrate rapidly in finite bath conditions according to eq. 2.3, then the ratio of t_{ch} for the fine/coarse mixture becomes (eq. 2.2/eq. 2.3):

$$\frac{t_{0.63,coarse}}{t_{0.63,fine}} = \frac{\frac{D_{aq}}{\delta}\frac{3}{r_{fine}\,\rho}\frac{m_{fine}}{V_w}}{\frac{D_{aq}}{\delta}\frac{3}{r_{coarse}\,\rho\, K_{d,coarse}}} \approx \left(\frac{r_{coarse}}{r_{fine}}\right)^2 K_{d,coarse}\frac{m_{fine}}{V_w} \tag{2.5}$$

Comparing eq. 2.1. and eq. 2.3 leads to the same result for large $K_{d,fine}$ values:

$$\begin{aligned}\frac{t_{0.63,coarse}}{t_{0.63,fine}} &= \frac{\frac{D_{aq}}{\delta}\frac{3}{\rho\, r_{fine}\, K_{d,fine}}\left(1 + K_{d,fine}\frac{m_{fine}}{V_w}\right)}{\frac{D_{aq}}{\delta}\frac{3}{r_{coarse}\,\rho\, K_{d,coarse}}} \\ &\approx \left(\frac{r_{coarse}}{r_{fine}}\right)^2 \frac{K_{d,coarse}}{K_{d,fine}}\left(1 + K_{d,fine}\frac{m_{fine}}{V_w}\right)\end{aligned} \tag{2.6}$$

Squared radii come in because for small Sherwood numbers (e.g., approaching 2) and δ decreases proportionally with decreasing radii of the particles (this also applies for intraparticle diffusion). Thus, already relatively small differences in particle size can make a big difference in the dynamics of equilibration kinetics in heterogeneous systems as already illustrated by Kleineidam et al. (1999); for more details see Liu, et al. (2022) [1]. These considerations also apply to redistribution scenarios, e.g., desorption from one particle class and sorptive uptake by the other; this typically applies for input of contaminated urban particles into rivers and redistribution of the pollutants to "native" less polluted particles and for passive sampling in aqueous suspensions.

[1] Liu et al. 2022. First order approximation for coupled film and intraparticle pore diffusion to model sorption/desorption batch experiments. https://doi.org/10.1016/j.jhazmat.2022.128314

Kleineidam et al. 1999: Impact of grain scale heterogeneity on slow sorption kinetics. https://doi.org/10.1002/etc.5620180810

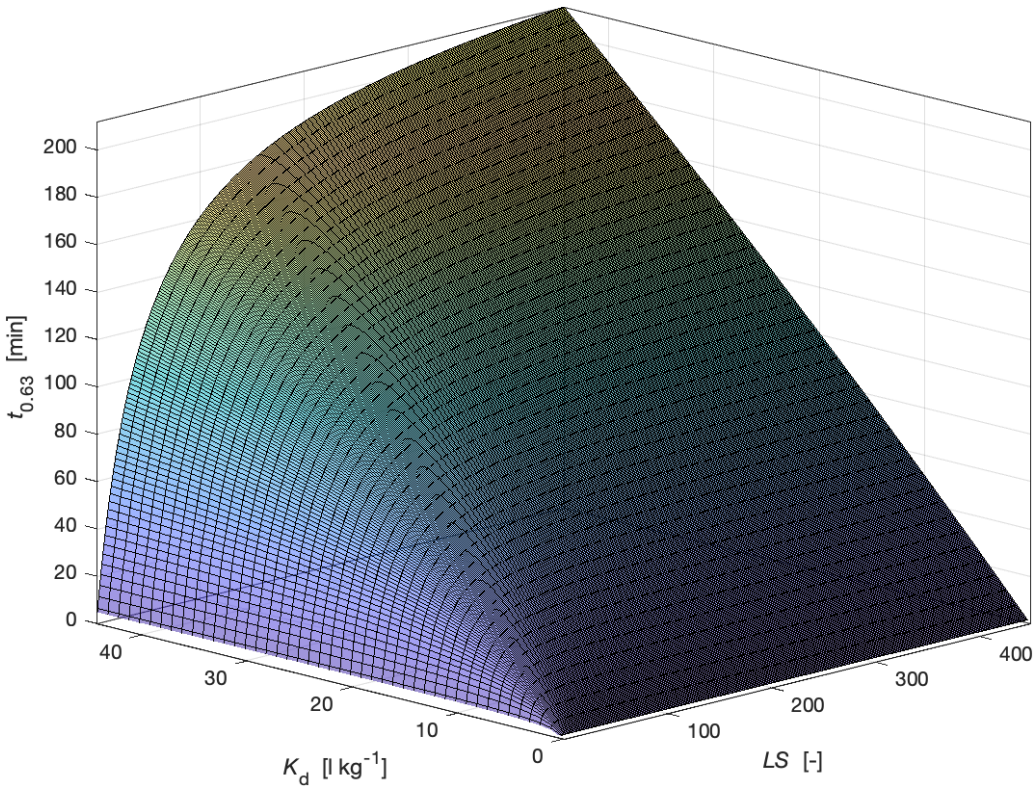


Fig. 2.2: Characteristic time to reach 63% of M/M_{eq} in a batch experiment (finite bath); grain size d = 1mm, Sh = 2 (see next chapter): LS (denotes the liquid/solid ratio (=V_w/m_d). For large LS (infinite bath), the characteristic time increases with increasing K_d while for K_d >> LS it increases with increasing LS (infinite sorbent); for heterogeneous systems LS accounts for V_w and a fast equilibrating (e.g., fine particle) fraction: $V_w + K_{d,fine}\, m_{fine}$ (instead of V_w alone we have V_w (1+ $K_{d,fine}\, m_{fine}/V_w$)).

3. SHERWOOD NUMBERS TO CALCULATE MASS TRANSFER COEFFICIENTS (OR FILM δ)

In order to get a realistic estimate of the characteristic equilibration time the mass transfer coefficient ($k = D_{aq}/\delta$) has to be known, which depends on the thickness of the aqueous boundary layer δ (see Fig. 1). δ is a function of the viscous forces in the liquid (e.g. water). In batch systems, it depends on shaking frequency and intensity, in percolation on the flow velocity of the water. δ can be estimated from empirical Sherwood numbers (Sh) which describe how k depends on diffusion coefficients, grain size (d) and δ:

$$\mathrm{Sh} = \frac{k\, d}{D_{aq}} = \frac{d}{\delta} \Rightarrow \delta = \frac{d}{\mathrm{Sh}} \tag{3.1}$$

In a first approximation δ may be estimated by introducing the mean square displacement (as used for the short term approximation of diffusion into a sphere at the end of this chapter):

$$\delta \approx \sqrt{\pi\, D_{aq}\, t_c} \approx \sqrt{\pi\, D_{aq} \frac{d}{v_a}} \tag{3.2}$$

where t_c denotes the unknown contact time of the water with the particle (the surface "renewal" time") which may be proportional to d/v_a (v_a is the velocity of water relative to the particle, i.e.

the advective velocity in a packed bed, the relative velocity in stirred or turbulent systems). With this, *Sh* becomes a function of the Peclet number (Pe):

$$\mathrm{Sh} = \frac{d}{\sqrt{\pi\, D_{aq}\frac{d}{v_a}}} = 0.56\sqrt{\frac{d\, v_a}{D_{aq}}} = 0.56\sqrt{\mathrm{Pe}}$$

$$\mathrm{Sh} \propto \sqrt{v_a \frac{d}{D_{aq}}} = \frac{\text{velocity}}{\text{mass transfer coefficient}} = \sqrt{\frac{v_a}{d}\frac{d^2}{D_{aq}}} = \frac{\text{diffusion time scale}}{\text{advection time scale}} \tag{3.3}$$

Since contact times (characteristic lengths and relative velocities) are not well known (and presumably in average much shorter than d/v_a), empirical relationships are used to correlate Sh and Pe. Liu et al. (2014) report a factor of 0.1 instead of 0.56 in eq. 3.3 for laminar flow in a packed bed; also the exponent may be slightly different form ½ (Fig. 2.1). The mass transfer coefficient k then increases with increasing diffusion coefficients and velocity and decreasing grain size (c here is an empirical constant):

$$k \approx c\sqrt{\frac{D_{aq}\, v}{d}} \tag{3.4}$$

The characteristic time then becomes:

$$t_{0.63} = \frac{K_d \rho\, d}{6\, c\sqrt{\frac{D_{aq}\, v}{d}}} = \frac{K_d \rho\, d^{3/2}}{6\, c\sqrt{D_{aq}\, v}} \tag{3.5}$$

and thus increases with $d^{3/2}$.

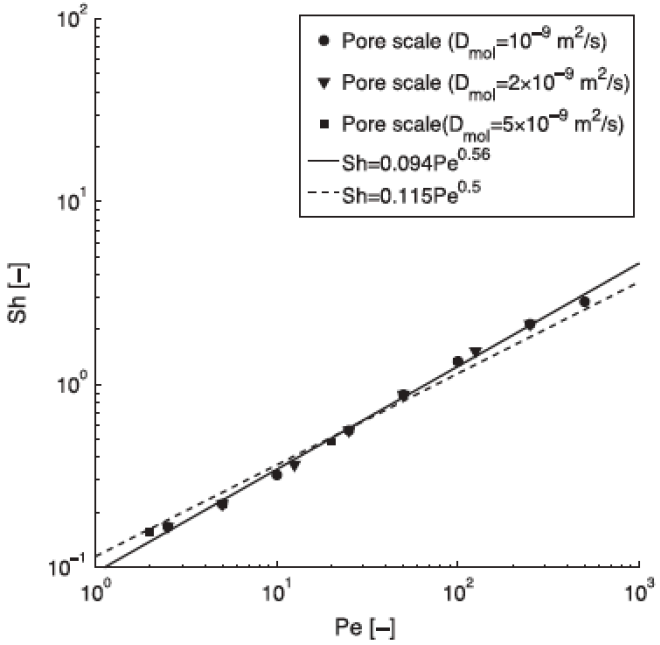


Fig. 2.1: Relationship between mass transfer (Sherwood number) and flow conditions (Peclet number) for compounds with different molecular diffusion coefficients inn water (from Liu et al., 2014). Sh = $k\, d/D_{aq}$ and Pe = $v\, d/D_{aq}$.

In real cases and especially turbulent systems mixing it is more complicated (e.g. the relative velocity increases with distance from the surface of the particle); for instance, if one assumes that the flow velocity itself becomes a function of the film thickness (e.g. normalized to the grain size: $v\, \delta/d$), then Sh depends on the 3rd root of Pe. As lower limit for Sh often 2 is reported, which can be derived for a sphere in stagnant water (or a small particle moving with the velocity of water) because the surface area available for diffusion increases with the distance squared and thus, the

maximum film thickness equals the radius of the sphere. Therefore, empirical relationships of following form are used (which also account for the viscosity, see Table 3.1):

$$\mathrm{Sh} = 2 + c\ \mathrm{Re}^{1/2}\ \mathrm{Sc}^{1/3} \tag{3.6}$$

where c is an empirical constant around 0.5. For packed beds with porosities of 0.4 - 0.5 (e.g. flow in porous media), where water flows around the spheres, Fitzer et al. (1995) report:

$$\mathrm{Sh} = 1.9\ \mathrm{Re}^{1/2}\ \mathrm{Sc}^{1/3} \tag{3.7}$$

Peclet (Pe), Schmidt (Sc) and Reynolds (Re) numbers are explained in Table 3.1. How mass transfer coefficients and thus characteristic times scale with grain size, diffusion coefficients or velocity depends on the empirical relationship chosen as shown in Table 3.2. Characteristic times for instance increase with increasing grain size, but depending on the Sherwood relationship with $d^{3/2}$, $d^{5/3}$ or d^2.

Box 3.1. Sh for diffusion from a "stagnant" sphere

Consider diffusion from a sphere (surface area: $4\ \pi\ d^2$) with a radius of r_{sp} (= $d/2$) into an infinite space we get for the total flux (D_m is the molecular diffusion coefficient):

$$F_{tot} = D_m\ \frac{dC}{dr}\ 4\ \pi\ r^2$$

The flux has to be the same at all distances from the surface of the sphere. Integration yields:

$$\int_{r_{sp}}^{\infty} \frac{F_{tot}\ dr}{4\ \pi\ r^2} = \int_{C_{sp}}^{C_\infty} D_m dC$$

$$\frac{F_{tot}}{4\ \pi}\left(\frac{1}{r_{sp}} - \frac{1}{r_\infty}\right) = D_m\left(C_\infty - C_{sp}\right)$$

$$F_{tot} = \frac{D_m}{\left(\frac{1}{r_{sp}}\right)} 4\ \pi\left(C_\infty - C_{sp}\right)$$

If this is normalized to the surface area of the sphere, then we get the flux density (which decreases with radial distance from the surface):

$$F = \frac{D_m}{4\ \pi\ r_{sp}^2\left(\frac{1}{r_{sp}}\right)} 4\ \pi\ \left(C_\infty - C_{sp}\right)$$

$$F = \frac{D_m}{r_{sp}}\ \left(C_\infty - C_{sp}\right) = -\frac{D_m}{d/2}\ \left(C_\infty - C_{sp}\right)$$

Thus, the film thickness at maximum becomes $d/2$ (= r_{sp}) and the **smallest Sherwood number is 2**.

Table 3.1: Dimensionless numbers used for calculation of mass transfer coefficients

Dimensionless Number (Group)	Physical Meaning	Used for
Sherwood number $\mathrm{Sh} = \frac{k\,d}{D}$ corresponds to Nusselt number in heat transfer	$\frac{mass\ transfer\ rate}{diffusion\ rate}$ or $\frac{characteristic\ length\ (d)}{boundary\ layer\ thickness\ (\delta)}$	Calculation of the mass transfer coefficient: $k = D/\delta$ [m/s])
Schmidt number $\mathrm{Sc} = \frac{\nu}{D}$ corresponds to Prandtl number in heat transfer	$\frac{viscous\ diffusion\ rate}{molecular\ diffusion\ rate}$ or $\frac{hydrodynamic\ layer}{mass\ transfer\ boundary\ layer}$	Ratio of kinematic viscosity ν * [$m^2\ s^{-1}$] and diffusion coefficient
Reynolds number $\mathrm{Re} = \frac{d\,v_a}{\nu}$	$\frac{inertial\ forces}{viscous\ forces}$	Above 2300 changes from laminar flow to turbulent flow
Peclet number $\mathrm{Pe} = \frac{d\,v_a}{D} = \mathrm{Re} \times \mathrm{Sc}$	$\frac{advective\ fluxes}{diffusive\ fluxes}$ or $\frac{time\ scale\ diffusion}{time\ scale\ advection}$	Relevance of advection compared to diffusion

*the kinematic viscosity is the dynamic viscosity η [Pa·s or N·s m^{-2} or kg/(m·s)] divided by the density ρ [kg m^{-3}] ($\nu = \eta/\rho$)

Table 3.2: Mass transfer coefficients and characteristic times for different Sherwood relationships

Sherwood number $\mathrm{Sh} = \frac{k\,d}{D}$	Mass transfer coefficient $k = \frac{\mathrm{Sh}\,D}{d}$	Characteristic time* $t_{0.63} = \frac{K_d\,\rho\,d}{6\,k}$
$= \mathrm{c}\sqrt{\mathrm{Pe}} = c\sqrt{\frac{d\,v_a}{D}}$	$= c\sqrt{\frac{d\,v_a}{D}}\frac{D}{d} = c\sqrt{\frac{D\,v_a}{d}}$	$= \frac{K_d\,\rho\,d}{6\,c\sqrt{\frac{D\,v_a}{d}}} = \frac{K_d\,\rho\,d^{3/2}}{6\,c\sqrt{D\,v_a}}$
$= \mathrm{c}\,\mathrm{Pe}^{1/3} = c\left(\frac{d\,v_a}{D}\right)^{1/3}$	$= c\left(\frac{d\,v_a}{D}\right)^{1/3}\frac{D}{d} = c\frac{D^{2/3}\,v_a^{1/3}}{d^{2/3}}$	$= \frac{K_d\,\rho\,d^{5/3}}{6\,c\,D^{2/3}\,v_a^{1/3}}$
$= \mathrm{c}\,\mathrm{Re}^{1/2}\,\mathrm{Sc}^{1/3}$ $= c\left(\frac{d\,v_a}{\nu}\right)^{1/2}\left(\frac{\nu}{D}\right)^{1/3}$	$= c\left(\frac{d\,v_a}{\nu}\right)^{1/2}\left(\frac{\nu}{D}\right)^{1/3}\frac{D}{d} = c\frac{D^{2/3}\,v_a^{1/2}}{d^{1/2}\,\nu^{1/6}}$	$= \frac{K_d\,\rho\,\nu^{1/6}\,d^{3/2}}{6\,c\,D^{2/3}\,v_a^{1/2}}$
$= 2$	$= 2\frac{D}{d}$	$= \frac{K_d\,\rho\,d^2}{6\,2\,D}$

c is an empirical constant

*in batch systems (finite bath) the characteristic times are divided by $1 + K_d\,m_d\,/V_w$ (then large K_d's drop out) and thus are shorter

4. FILM DIFFUSION WITH FIXED SURFACE MASS TRANSFER RESISTANCE

Analogous to the first chapter we can derive diffusion into (or out of) a sphere, e.g. a microplastic particle, resin beads or even liquids which is limited by a fixed solid (or liquid) layer ("shell") of the same material with thickness δ. For uptake or release in the infinite bath the external concentration in water or gas phase is fixed (either at equilibrium or 0) resulting in constant concentration at the surface of the sphere ($C_s = C_{s,eq}$ or 0) and eq. 1.5 may be expressed as:

$$\frac{\partial C_s}{\partial t} = -\frac{D_s}{\delta}\frac{3}{r}\left(C_s - C_{s,eq}\right) \tag{4.1}$$

or for desorption

$$\frac{\partial C_s}{\partial t} = -\frac{D_s}{\delta}\frac{3}{r}(C_s - 0)$$

D_s is the diffusion coefficient in the surface layer; furthermore δ is small compared to r and the layer does not store the solute. $3/r$ is the specific surface area (surface per volume of a sphere). Integration yields the following analytical solutions for uptake:

$$\int_0^{C_s} \frac{\partial C_s}{C_s - C_{s,eq}} = \int_0^{t} -\frac{D_s}{\delta}\frac{3}{r}\partial t \tag{4.2}$$

$$\ln\left(C_s - C_{s,eq}\right) - \ln\left(-C_{s,eq}\right) = \ln\left(-\frac{C_s}{C_{s,eq}} + 1\right) = -\frac{D_s}{\delta}\frac{3}{r}t$$

$$\frac{C_s}{C_{s,eq}} = 1 - \exp\left(-\frac{D_s}{\delta}\frac{3}{r}t\right)$$

or more generally which also applies for desorption:

$$\frac{M}{M_{eq}} = 1 - \exp\left(-\frac{D_s}{\delta}\frac{3}{r}t\right)$$

=> in the infinite bath sorption/desorption time scales are independent on K_d, if mass transfer limitations are inside a nonporous, solid particle

More frequent, especially in laboratory batch experiments, is the finite bath boundary condition:

$$\frac{\partial C_s}{\partial t} = -\frac{D_s}{\delta}\frac{3}{r}\left(C_s - C_s'\right) \tag{4.3}$$

The unknown concentration at the surface C'_s is in equilibrium with the aqueous concentration C_w (= C'_s/K_d). C_w is calculated from the total mass in the system which under equilibrium conditions is simply given by the sum present in the water and the solids ($C_{s,eq}\, m_d + C_{w,eq}\, V_w$) minus the actual mass in the solids ($C_s\, m_d$).

$$C_w = \frac{C_{w,eq}V_w + C_{s,eq}\, m_d - C_s m_d}{V_w} = C_{w,eq} + C_{s,eq}\,\frac{m_d}{V_w} - C_s\,\frac{m_d}{V_w}$$

C'_s thus is:

$$\begin{aligned} C'_s = K_d\, C_w = {} & C_{w,eq}K_d + C_{s,eq}K_d\,\frac{m_d}{V_w} - C_s K_d\,\frac{m_d}{V_w} \\ = {} & C_{s,eq} + C_{s,eq}K_d\,\frac{m_d}{V_w} - C_s K_d\,\frac{m_d}{V_w} \end{aligned} \tag{4.4}$$

The concentration difference in 4.3 then becomes:

$$\begin{aligned} C_s - C'_s &= C_s - C_{s,eq} - C_{s,eq}K_d\,\frac{m_d}{V_w} + C_s K_d\,\frac{m_d}{V_w} \\ &= C_s\left(1 + K_d\,\frac{m_d}{V_w}\right) - C_{s,eq}\left(1 + K_d\,\frac{m_d}{V_w}\right) \end{aligned} \tag{4.5}$$

Thus eq. 4.3 becomes:

$$\frac{\partial C_s}{\partial t} = -\frac{D_s}{\delta}\frac{3}{r}\left(1 + K_d\,\frac{m_d}{V_w}\right)\left(C_s - C_{s,eq}\right) \tag{4.6}$$

which upon integration yields the following analytical solution (sorption mode - initial condition $C_{s\,(t=0)} = 0$):

$$\int_0^{C_s} \frac{\partial C_s}{C_s - C_{s,eq}} = \int_0^{t} -\frac{D_s}{\delta}\frac{3}{r}\left(1 + K_d\,\frac{m_d}{V_w}\right)\partial t \tag{4.7}$$

$$\ln\left(C_s - C_{s,eq}\right) - \ln\left(0 - C_{s,eq}\right) = \ln\left(-\frac{C_s}{C_{s,eq}} + 1\right) = -\frac{D_s}{\delta}\frac{3}{r}\left(1 + K_d\,\frac{m_d}{V_w}\right)t$$

and for the relative mass which has diffused into or out of the sphere:

$$\frac{M}{M_{eq}} = 1 - \exp\left(-\frac{D_s}{\delta}\frac{3}{r}\left(1 + K_d\,\frac{m_d}{V_w}\right)t\right)$$

Thus, with increasing sorption (K_d) sorption kinetics limited by diffusion in a solid in batch systems always gets accelerated (if $K_d\, m_d/V_w > 1$).

=> in the finite bath sorption/desorption time scales are decreasing with increasing K_d (and increasing solid to liquid ratios) if mass transfer limitations are inside a nonporous, solid particle (e.g. microplastic)

Increasing the internal film thickness with time during intraparticle diffusion.

If we assume internal mass transfer resistance such as intraparticle diffusion, δ in eq. 4.6 and 4.3 may be estimated by the mean square displacement (= diffusion distance, here $(\pi\, D_s\, t)^{0.5}$) which grows with the square root of time:

$$\frac{\partial C_s}{\partial t} = -\frac{D_s}{\sqrt{\pi\, D_s\, t}}\frac{3}{r}\left(1 + K_d\,\frac{m_d}{V_w}\right)\left(C_s - C_{s,eq}\right) \tag{4.7}$$

The solution for early times ($C_s << C_{s,eq}$) may be easily obtained upon integration (with $C_s \approx 0$):

$$\int_0^{C_s} \frac{\partial C_s}{C_{s,eq}} = \int_0^t \frac{3}{r}\left(1 + K_d \frac{m_d}{V_w}\right)\sqrt{\frac{D_s}{\pi\, t}}\; dt \qquad (4.8)$$

$$\frac{M}{M_{eq}} = 2\,\frac{3}{r}\left(1 + K_d \frac{m_d}{V_w}\right)\sqrt{\frac{D_s\, t}{\pi}}$$

This corresponds exactly to the early time solution for intraparticle diffusion (see next chapter) with the difference that diffusion in the solid is independent on K_d (for large K_ds and or low liquid to solid ratios, kinetics accelerates with K_d and m_d/V_w squared). This approximation only holds for low $C_w/C_{w,eq}$ (< 0.5). An approximation working for longer times is obtained if we directly integrate eq. 4.7:

$$\int_0^{C_s} \frac{\partial C_s}{C_s - C_{s,eq}} = \int_0^t \frac{3}{r}\left(1 + K_d \frac{m_d}{V_w}\right)\sqrt{\frac{D_s}{\pi\, t}}\; dt \qquad (4.9)$$

$$\frac{M}{M_{eq}} = 1 - \exp\left(-2\frac{3}{r}\left(1 + K_d \frac{m_d}{V_w}\right)\sqrt{\frac{D_s\, t}{\pi}}\right)$$

Note, for small arguments (x), 1-exp(-x) may be approximated by x which leads again to eq. 4.8. These solutions are obtained by inserting $(\pi\, D_s\, t)^{0.5}$ directly in eq. 4.7.

5. PRACTICAL APPLICATION: PASSIVE SAMPLING

Understanding mass transfer through layers of given thicknesses may be applied to design passive samplers for monitoring of pollutants in the environment. The advantages of passive sampling in the field are i) that no samples (water or air) have to be taken which often introduces artifacts such as loss of the target compound or cross-contamination and ii) sampling integrates over a certain time period and provides an average concentration which is an advantage if concentrations in the environment fluctuate (only one "passive" sample is requires instead of many samples to get a robust average).

Passive sampling in the environment comes in many different designs, the most frequent is using organic polymers to collect organic pollutants in air or water – in fact, natural organic matter in soils and sediments and even plants (leaves, bark, wood) may be considered as passive samplers, same for microplastic particles in the environment. For calibration and selecting the proper monitoring time period the mass transfer mechanisms of target compounds into the passive sampler have to be understood. Here we introduce the design of a "dosimeter" for sampling of pollutants in water, which involves diffusion of the target compound through a porous membrane of given thickness into an adsorbent which acts as infinite sink (Martin et al., 2001, 2003). As illustrated in Fig. 5.1., this is realized by a hollow ceramic cylinder ("membrane") which contains a suitable sorbent for the target compounds (polymers or activated carbon for organic compounds). Diffusion into the sorbent material is limited by diffusion in the ceramic membrane; the effective diffusion coefficient (D_{mem}) may be estimated by empirical relationships similar to the well-known Archie's law correlation:

$$D_{mem} = D_w \varepsilon^m \qquad (5.1)$$

The empirical exponent m accounts for the tortuosity and is mostly between 1.5 and 2, but for analytical purposed the value for m has to be calibrated.



Fig. 5.1: Design of a ceramic passive sampler "dosimeter" (Bopp et al., 2004; Weiß et al., 2007)

Fluxes. The total flux of the target compound into the ceramic cylinder depends on the surface area ($2\ \pi\ r\ l$) and the inner and outer radii of the cylinder membrane (r_{out}, r_{in}) have to be considered; the total flux then is (note similarities in calculating film thicknesses and Sherwood numbers for spheres):

$$F_{tot} = D_{mem} 2\,\pi\, r\, l\, \frac{dC}{dr} \tag{5.2}$$

$2\,\pi\, r\, l$ is the area of a cylinder with length l. Integration yields:

$$\int_{r_{out}}^{r_{in}} \frac{F_{tot}\, dr}{2\,\pi\, r\, l} = \int_{C_{out}}^{C_{in}} D_{mem} dC$$

$$\frac{F_{tot}}{2\,\pi\, l}(\ln r_{out} - \ln r_{in}) = D_{mem}(C_{out} - C_{in}) \tag{5.3}$$

$$F_{tot} = D_{mem} 2\,\pi\, l\, \frac{(C_{out} - C_{in})}{\ln\left(\frac{r_{out}}{r_{in}}\right)}$$

Dividing by the surface area yields the flux density and illustrates the effective membrane thickness:

$$F = \frac{D_{mem}}{r_{in} \ln\left(\frac{r_{out}}{r_{in}}\right)}(C_{out} - C_{in}) \tag{5.4}$$

Often following simplification is used (just based on the thickness of the membrane):

$$F_{tot} = \frac{D_{mem} 2\,\pi\, l\, r_{out}}{r_{out} - r_{in}}(C_{out} - C_{in}) = \frac{D_{mem} 2\,\pi\, l}{1 - \left(\frac{r_{in}}{r_{out}}\right)}(C_{out} - C_{in}) \tag{5.5}$$

This compares well to eq. 5.3 for ratios of r_{in}/r_{out} close to one (e.g. > 0.8), then $1 - r_{in}/r_{out} \approx \ln r_{out}/r_{in}$.

Target compound uptake and characteristic times. The change of concentration (C_s) of the target compound in the adsorber material inside the dosimeter is:

$$\frac{dC_s}{dt} = \frac{D_{mem} 2\,\pi\, l}{m_d} \frac{(C_{out} - C_{in})}{\ln\left(\frac{r_{out}}{r_{in}}\right)} = \frac{D_{mem} 2\,\pi\, l}{m_d} \frac{\left(\frac{C_{s,eq}}{K_d} - \frac{C_s}{K_d}\right)}{\ln\left(\frac{r_{out}}{r_{in}}\right)} \tag{5.6}$$

K_d is the distribution coefficient between adsorber material of mass m_d and water. $C_{s,eq}/K_d$ is the average concentration in water outside the dosimeter (or the arithmetic average of it), C_s/K_d is the aqueous concentration inside the dosimeter. The analytical solution for this is:

$$\frac{C_s}{C_{s,eq}} = 1 - \exp\left(-\frac{D_{mem} 2\,\pi\, l}{K_d\, m_d\, \ln\left(\frac{r_{out}}{r_{in}}\right)}\, t\right) \tag{5.7}$$

K_d is the distribution coefficient between adsorber mass (m) and water. $C_{s,eq}/K_d$ is the concentration. The term before the time is the rate constant and the inverse of that is a characteristic time:

$$t_{char} = \frac{K_d\, m_d\, \ln\left(\frac{r_{out}}{r_{in}}\right)}{D_{mem} 2\,\pi\, l} \tag{5.8}$$

The absolute mass in the adsorber as a function of the concentration of the target compound in water is:

$$M_s = C_w\, K_d\, m_d \left[1 - \exp\left(-\frac{D_{mem} 2\,\pi\, l}{K_d\, m_d\, \ln\left(\frac{r_{out}}{r_{in}}\right)}\, t\right)\right] \tag{5.9}$$

For small arguments of the exponential function (early time) the uptake is linear and proportional to the negative argument:

$$M_s = C_w\, K_d\, m_d\, \frac{D_{mem} 2\,\pi\, l}{K_d\, m_d\, \ln\left(\frac{r_{out}}{r_{in}}\right)}\, t = C_w \frac{D_{mem} 2\,\pi\, l}{\ln\left(\frac{r_{out}}{r_{in}}\right)}\, t \qquad (5.10)$$

Thus, in this range (far away from equilibrium) uptake is independent on K_d and mass of adsorbent and the same for all compounds (see for illustration Fig. 5.2). This is the desired operation state of a dosimeter (or general a non-equilibrium passive sampler).

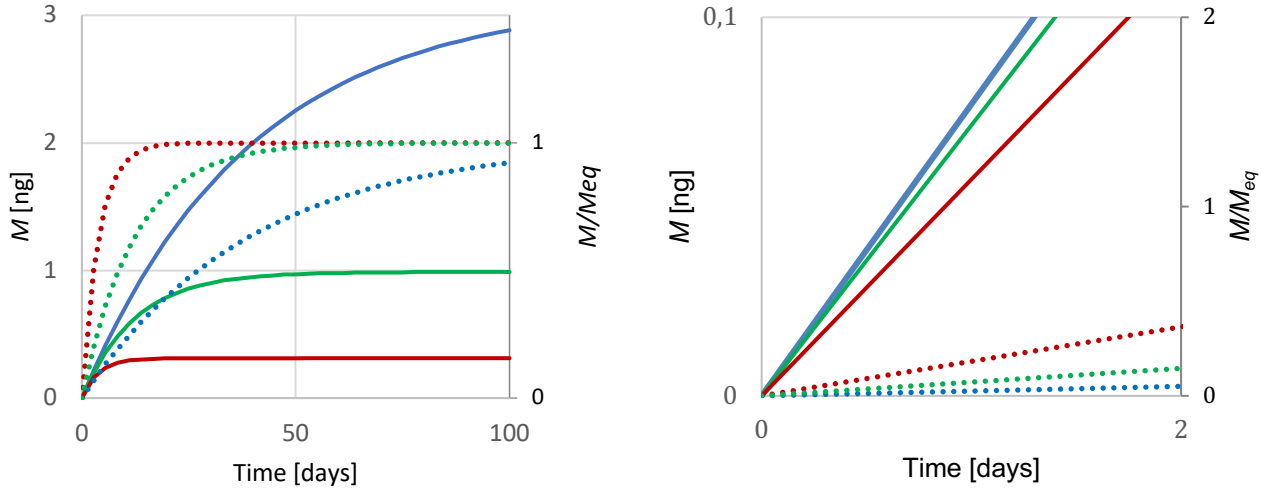


Fig. 5.2: Mass uptake in Dosimeter in ng (solid lines) and relative uptake (dotted lines) at different K_d-values (low: red, high: blue); initially absolute mass uptake (M) is (almost) independent on K_d as shown in the right plot (solid lines) while relative mass M/M_{eq} depends on K_d – as in all first order sorptive uptake processes in an infinite bath.

Calibration in batch studies. In a sorptive uptake experiment in a bottle (batch test) the initial high concentration in water ($C_{w,0}$) drops to the equilibrium concentration ($C_{w,eq}$):

$$\frac{C_w - C_{w,eq}}{C_{w,0} - C_{w,eq}} = \exp\left(-k\, A^o \left(1 + \frac{V_w}{K_d\, m_d}\right) t\right) \qquad (5.11)$$

$k\,A^0$ is a rate constant (i.e. the product of the mass transfer coefficient and the specific surface area of the dosimeter to the volume of water V_w):

$$k\, A^o = \frac{D_{mem} 2\,\pi\, l}{\ln\left(\frac{r_{out}}{r_{in}}\right) V_w} = \frac{D_{aq}\, \varepsilon^m\, 2\,\pi\, l}{\ln\left(\frac{r_{out}}{r_{in}}\right) V_w} \qquad (5.12)$$

Since the aqueous diffusion coefficient (D_{aq}) and the porosity of the membrane (ε) are known, the exponent m is the only fitting factor. If $C_{w,eq}$ goes to zero, then we get a simple exponential decay:

$$\frac{C_w}{C_{w,0}} = \exp\left(-\frac{D_{aq}\, \varepsilon^m}{\ln\left(\frac{r_{out}}{r_{in}}\right)} 2\,\pi\, l \left(\frac{1}{V_w} + \frac{1}{K_d\, m_d}\right) t\right) \qquad (5.13)$$

If K_d gets big then it drops out and we simply arrive at:

$$\frac{C_w}{C_{w,0}} = \exp\left(-\frac{D_{aq}\, \varepsilon^m}{\ln\left(\frac{r_{out}}{r_{in}}\right)} \frac{2\,\pi\, l}{V_w} t\right) \qquad (5.14)$$

In this case m may be determined by linear regression in a semi-log plot.

6. SUMMARY

"Take home messages" on K_d dependency of sorption/desorption kinetics

- **Film diffusion in an external boundary layer** (e.g., water or air film): Slows down with increasing K_d in the infinite bath but becomes independent on K_d in the finite bath for large K_d values (still depends on the liquid to solid ratios; faster with increasing $m_d/V_w = 1/LS$)
- If sorptive uptake is expressed as $K_{d,a}/K_d$ then kinetics at early times appear independent on the liquid to solid ratio (LS)
- **Intraparticle diffusion** (e.g., diffusion in a solid particle such as a polymer sphere): Independent of K_d in the infinite bath but accelerates in the finite bath with increasing K_d (at early times with K_d squared) - **Intraparticle pore diffusion** slows down with increasing K_d in the infinite bath, but in the finite bath gets accelerated with increasing K_d (next chapter)

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