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MASS DIFFUSION

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MASS TRANSFER

WHAT IT IS AND WHAT IT ISN'T

The subject of Mass Transfer studies the relative motion of some chemical species with respect to others (i.e. separation and mixing processes), driven by concentration gradients (really, an imbalance in chemical potential, as explained in [Entropy](#)). Fluid flow without mass transfer is not part of the Mass Transfer field but of Fluid Mechanics.

Heat transfer and mass transfer are kinetic processes that may occur and be studied separately or jointly. Studying them apart is simpler, but it is most convenient (to optimise the effort) to realise that both processes are modelled by similar mathematical equations in the case of diffusion and convection (there is no mass-transfer similarity to heat radiation), and it is thus more efficient to consider them jointly. On the other hand, the subject of Mass Transfer is directly linked to Fluid Mechanics, where the single-component fluid-flow is studied, but the approach usually followed is more similar to that used in Heat Transfer, where fluid flow is mainly a boundary condition empirically modelled; thus, the teaching of Mass Transfer traditionally follows and builds upon that of [Heat Transfer](#) (and not upon Fluid Mechanics). In fact, development in mass-transfer theory closely follows that in heat transfer, with the pioneering works of Lewis and Whitman in 1924 (already proposing a mass-transfer coefficient h_m similar to the thermal convection coefficient h), and Sherwood's book of 1937 on "Absorption and extraction". Even more, since the milestone book on "Transport phenomena" by Bird et al. (1960), heat transfer, mass transfer, and momentum transfer, are often jointly considered as a new discipline.

As usual, the basic study first focuses on homogeneous non-reacting systems with well-defined boundaries (not only in Mass Transfer, but in Heat Transfer and in Fluid Mechanics), touching upon moving-boundary problems and reacting processes only afterwards. As for the other subjects, it is based on the continuum media theory, i.e. without accounting for the microscopic motion of the molecules (so that field theory and the fluid-particle concept are applied here too). Diffusion theory only applies to molecular mixtures ($d < 10^{-8}$ m); for [colloids and suspensions](#) ($10^{-8}..10^{-5}$ m), Brownian theory must be applied, and for larger particles ($>10^{-5}$ m) Newtonian mechanics applies.

Notice that we only consider here mass diffusion due to a concentration gradient, what might be called concentration-phoresis in analogy to other mechanisms of mass diffusion like thermo-phoresis (Soret effect), piezo-phoresis (diffusion due to a pressure gradient), or electrophoresis (diffusion due to a gradient of electrical potential applied to ionic media).

Traditionally, the field of Mass Transfer has been studied only within the Chemical Engineering curriculum, except for humid-air applications (evaporation) and thermal desalination processes, which has been always studied in Mechanical Engineering. But mass transfer problems are proliferating in so many circumstances, especially at high temperatures (drying, combustion, materials treatment, pyrolysis, ablation...), that the subject should be covered on different grounds to encourage effective interdisciplinary team-work

WHAT IT IS FOR. APPLICATIONS

Applications of Mass Transfer include the dispersion of contaminants, drying and humidifying, segregation and doping in materials, vaporisation and condensation in a mixture, evaporation (boiling of a pure substance is not mass transfer), combustion and most other chemical processes, cooling towers, sorption at an interface (adsorption) or in a bulk (absorption), and most living-matter processes as respiration (in the lungs and at cell level), nutrition, secretion, sweating, etc.

A common process to separate a gas from a gaseous mixture is to selectively dissolve it in an appropriate liquid (this way, carbon dioxide from exhaust gases can be trapped in aqueous lime solutions, and hydrogen sulfide is absorbed from natural-gas sources; when water vapour is removed, the absorption process is called drying. Stripping is the reverse of absorption, i.e. the removal of dissolved components in a liquid mixture. Distillation is the most important separation technique.

HOW TO STUDY IT. SIMILARITIES AND DIFFERENCES BETWEEN MASS TRANSFER AND HEAT TRANSFER

Mass Transfer education traditionally follows and builds upon that of Heat Transfer because, on the one hand, mass diffusion due to a concentration gradient is analogous to thermal-energy diffusion due to a temperature gradient, and thus the mathematical modelling practically coincides, and there are many cases where mass diffusion is coupled to heat transfer (as in evaporative cooling and fractional distillation); on another hand, Heat Transfer is mathematically simpler and of wider engineering interest than Mass Transfer, what dictates the precedence. But there are important differences between both subjects.

- Radiation. First of all, from the three heat transfer modes (conduction, convection, and radiation), only the two first are considered in mass transfer (diffusion and convection), radiation of material particles (as neutrons and electrons) being studied apart (in Nuclear Physics). Notice, by the way, that the word diffusion can be applied to the spreading of energy (heat diffusion), or species (mass diffusion), or even momentum in a fluid or electric charges in conductors, but the word conduction is more commonly used than heat diffusion (whereas mass conduction is rarely used).
- Solids versus fluids. Heat Transfer starts with, and focuses on, heat diffusion in solids, which have higher thermal conductivities than fluids, the latter being considered globally through empirical convective coefficients, whereas Mass Transfer focuses on gases and liquids, which have higher mass diffusivities than solids. The explanation for such a difference is that heat conduction propagates by particle contact (for the same type of particles, the shortest separation the better), whereas mass diffusion propagates by particles moving through the material medium (for the same type of particles, the largest voids the better). Moreover, Heat Transfer problems in solids are simple and relevant to many applications, whereas Mass Transfer problems in solids are of much lesser relevance, and Mass Transfer problems in fluids are much more complicated because the simplest mass-diffusion problems are of little practical interest, convection within fluids being the rule (fluids tend to flow). When diffusion in solids is wanted, as in doping silicon substrates in microelectronics, or in surface diffusion of carbon or nitrogen in steel hardening, high temperature operation is the rule (diffusion coefficients show an Arrhenius' type dependence with temperature).
- Slowness. Thermal diffusivities decrease from solids to fluids, with typical values of $a \approx 10^{-4}$ m²/s for metals and $a \approx 10^{-5}$ m²/s for non-metals, down to $a \approx 10^{-5}$ m²/s for gases and $a \approx 10^{-7}$ m²/s for liquids. On the contrary, mass diffusivities decrease from fluids to solids, with typical values of $D_i \approx 10^{-5}$ m²/s for gases and $D_i \approx 10^{-9}$ m²/s for liquids, down to $D_i \approx 10^{-12}$ m²/s for solids.
- Bulk flow. There is no bulk flow in heat diffusion (either within solids or fluids), whereas there is always some bulk flow associated to diffusion of species (except in the rare event of counter-diffusion of similar species); i.e. mass diffusion generates mass convection, in general.
- Number of field variables. One may consider just one heat-transfer function, the temperature field T (the heat flux is basically the gradient field), but several mass-transfer functions must be considered, one mass fraction, y_i , for each species $i=1..C$ (C being the number of distinct chemical species), although most problems are modelled as a binary system of just one species of interest diffusing in a background mixture of averaged properties.
- Continuity at interfaces. Mass-transfer boundary conditions at interfaces are more complex than thermal boundary conditions, because there are always concentration discontinuities, contrary to the continuous temperature dictated by local equilibrium (chemical potentials are continuous at an interface, not concentrations).
- Diffusion 'uphill'. Besides the effect of coupled fluxes, it is important to realise that mass diffusion can be from a low concentration within a condensed medium towards a high concentration within a more disperse medium, because, as said, it is not concentration-gradient but chemical-potential-gradient, what drives mass diffusion (e.g. see Diffusion through a wall, below).

Forces and fluxes

Mixing, i.e. decreasing differences in composition (really, in chemical potential) or temperature, is a natural process (i.e. it does not require an energy expenditure), driven by the gradients of temperature, relative speed and chemical composition (with the natural stratification in the presence of gravity or another force field).

It is interesting to realise that the thermal and mechanical forces towards equilibrium have been harnessed to yield useful power (heat engines, wind and water turbines), but the chemical forces that drive mass transfer have not yet been rendered useful as energy source, no doubt because of its low specific energy (there has been proposals to built power plants driven by the difference in salt concentration at river mouths).

The gradient of temperature, momentum and concentrations, give rise to corresponding fluxes in thermal energy, momentum and amount of species. The relation between forces and fluxes are the transport constitutive equations: Fourier law for Heat Transfer, Newton (or Stokes) law for Fluid Mechanics, and Fick law for Mass Transfer (to be presented below), and the purpose of the subject is to solve generic field balance equations (energy balance, momentum balance, and species balance), with the help of constitutive equations, and the particular boundary conditions and initial conditions.

But before developing the theory, it must be understood that mixing is a slow physical process, if not forced by convection and turbulence, and even so. Many practical processes are limited by the difficulty to increase the mass transfer rate. An order of magnitude analysis shows that the relaxation time for diffusion-controlled phenomena (thermal, momentum, species) across a distance L is $t_{\text{relax}}=L^2/a$, where a is the diffusivity that, as explained below, is of order 10^{-5} m²/s in gases, what teaches that diffusion across a 1 m distance takes some 10^5 s, i.e. one whole day. Of course, everybody knows that heating one metre of air doesn't take one day, neither it takes so long for odours to travel one metre, or for putting in motion or arresting a gas; the explanation is that fluids are very difficult to keep at rest when perturbed, and the convection that develops greatly increases the mixing rate and lowers the required time.

Thermodynamics teaches that, within an isolated system in absence of external forces, temperature, relative motion and chemical potential tend to get uniform, by establishing a thermal-energy flux, a momentum flux and a mass-diffusion flux, proportional (to a first approximation) to the gradients of temperature, velocity and concentration, that tend to equilibrate the system. Notice however that, besides those direct fluxes, other smaller cross-coupling fluxes may appear, as mass-diffusion due to a temperature gradient in a uniform concentration, or heat transfer due to a concentration gradient in an isothermal field, which, in the linear approximation, are related among them by Onsager's reciprocal relations.

Specifying composition. Nomenclature

Mass transfer may take place within gases, liquids, solids or through their interfaces, always involving a mixture, but mass diffusion in a gas is of main interest for two reasons: first, it is the best understood, and

second, it is the best diffusing medium (diffusion in liquids and solids is much slower). For that reason, and for simplicity, we start here with a gaseous (single phase) multi-component mixture.

A mixture is any multi-component system, i.e. one with several chemical species. The thermodynamics of mixtures in general (gaseous, liquid or solid) has been considered under the heading [Mixtures](#), mainly devoted to ideal mixtures. We assume true solutions, i.e. homogeneous solutions, and do not consider colloids and suspensions, treated under the heading [Mixture settling](#).

Although, from the theoretical point-of-view, molar fractions and concentrations should be preferred, the most common composition determinant in a single-phase mixture is the mass fraction, y_i , or the mass density ρ_i . Only one of those parameters is needed, but all of them are made use of in practice, so a common (an tedious) task in mass-transfer calculations is to pass from one variable to another, based on their definitions:

$$\text{mass fractions: } y_i \equiv \frac{m_i}{\sum m_i} = \frac{x_i M_i}{\sum x_i M_i} \quad (1)$$

$$\text{mass densities (or mass concentrations): } \rho_i \equiv \frac{m_i}{V} = y_i \rho \quad (2)$$

$$\text{molar densities (or molar concentrations): } c_i \equiv \frac{n_i}{V} = \frac{\rho_i}{M_i} = \frac{x_i}{\sum x_i M_i} \rho \quad (3)$$

$$\text{molar fractions: } x_i \equiv \frac{n_i}{\sum n_i} = \frac{y_i / M_i}{\sum y_i / M_i} \quad (4)$$

$$\text{partial pressure of a species } i \text{ in a gas mixture: } p_i \equiv x_i p \stackrel{\text{IGM}}{=} c_i R_u T = \rho_i \frac{R_u}{M_i} T. \quad (5)$$

The molar mass of the mixture is defined as $M_m \equiv m/n = \rho/c = \sum x_i M_i$, although it is only used for gas mixtures. There are still other special variables in use to define a mixture composition, as air-to-fuel ratio and richness (equivalence ratio) in combustion problems.

Exercise 1. Dry air can be approximated as a mixture of 79% N₂ and 21% O₂ by volume (meaning that, by letting 79 volumes of pure nitrogen to mix with 21 volumes of pure oxygen, without changes in pressure and temperature, i.e. by just removing the partition, we obtain 100 volumes of a mixture closely resembling dry air). Determine other possible specifications of dry air composition, from (1-5).

Solution. Assuming ideal gas behaviour, i.e. $pV=nRT$, at constant p and T , volumes V are proportional to amounts of substance, n , and thus volume percentage coincides with molar fractions (4); i.e., we can consider as data $x_N=0.79$ and $x_O=0.21$ (mind that subindices are just labels, not meaning atoms but molecules).

From (1), with $M_N=0.028$ kg/mol and $M_O=0.032$ kg/mol, one gets $\sum x_i M_i = 0.79 \cdot 0.028 + 0.21 \cdot 0.032 = 0.029$ kg/mol, $y_N = 0.79 \cdot 0.028 / 0.029 = 0.77$ and $y_O = 0.23$, indicating that the molar mass for the mixture is a weighted average of those of the

components, $M_m \equiv m/n = \rho/c = \sum x_i M_i = 0.029 \text{ kg/mol}$, and that the heavier species shows a larger concentration-value in terms of masses than in terms of amounts of substance.

From (2) we get mass concentrations (mass densities) in terms of the mixture density, which depends on temperature and pressure; for $T=288 \text{ K}$ and $p=100 \text{ kPa}$, we get for the density of air $\rho=1.21 \text{ kg/m}^3$, and for the species $\rho_N=0.77 \cdot 1.22=0.93 \text{ kg/m}^3$, and $\rho_O=0.23 \cdot 1.22=0.28 \text{ kg/m}^3$. Notice that some authors use m_i or w_i instead of y_i for mass fractions.

From (3) we can get molar concentrations, again depending on actual p - T values; with the previous choice, $c_N=\rho_N/M_N=0.93/0.028=33 \text{ mol/m}^3$, and $c_O=\rho_O/M_O=0.28/0.032=9 \text{ mol/m}^3$ (in total, $c=c_N+c_O=p/(RT)=10^5/(8.3 \cdot 288)=42 \text{ mol/m}^3$).

From (5) we get the partial pressures, $p_N=x_N p=0.79 \cdot 10^5=79 \text{ kPa}$, and $p_O=x_O p=0.21 \cdot 10^5=21 \text{ kPa}$. Finally notice that we can equally say that air has $0.79/0.21=3.76$ times more nitrogen than oxygen, by volume (or amount of substance), or $0.77/0.23=3.29$ times more nitrogen than oxygen, by mass.

The finding of qualitative or quantitative composition in a mixture is known as chemical analysis, or simply 'the analysis'. We focus here on quantitative analysis, assuming the substances are already known. Most methods of concentration analysis are based on measuring mixture density (provided the density dependence on species concentration, $\rho_m=\rho_m(T,p,x_i)$, is known beforehand by calibration), by one of the different techniques:

- Absorption radiometry. By light transmittance (in the visible, infrared, or monochromatic).
- Refractometry. By ray tracing. Refractive index varies almost linearly with density.
- Gravimetry. Weighting a known volume of liquid. This is perhaps the easiest and quickest method to measure solution concentration, but requires sampling.
- Resonant vibration. The natural frequency of an encapsulated liquid sample precisely metered depends on its mass. May be applied to a liquid flowing along a bend connected by soft bellows to the pipes.
- Sonic velocimetry. Density is obtained from $\rho=E/c^2$, where E is the bulk modulus of the solution and c the sound speed through it.
- Electric conductivity. This is the best method for very low concentration of electrolytic solutions. The measuring electrodes may be generic, or selective for some specific ion (e.g. Ca^{2+} , NH_4^+ , Cl^- , NO_3^-).

Specifying boundary conditions for composition

Composition at boundaries or internal interfaces in a mixture usually shows a discontinuity, contrary to temperature in heat transfer problems, when continuity is the rule (except for the special topic of thermal joint conductance).

The typical boundary conditions for a species concentration are, as for heat transfer, a known value of the function (imposed concentration or temperature, respectively), or a known value of its gradient (imposed species flux or heat flux, respectively), the special case in the latter being the impermeable interface or adiabatic wall, respectively; here:

$$\text{impermeable interface: } \nabla x_i \cdot \vec{n} = 0, \quad \text{or in 1D } \left. \frac{\partial x_i}{\partial x} \right|_{x=x_{\text{interface}}} = 0 \quad (6)$$

\vec{n} being the unit normal vector to the interface. Imposing a non-zero mass flux, or a given concentration value, is done as in Heat Transfer, i.e. by providing large sources of the chemical species (a solid chunk, a liquid pool, a gas reservoir), similarly to large metal blocks to specify the temperature at a wall. Local thermodynamic equilibrium then teaches that the temperature of the system near the wall is equal to that of the wall, but the same is not true for concentrations, where local equilibrium implies equality of its chemical potential, not of its concentration.

The boundary condition in a gas mixture may be another gas phase, as when mixing along a tube connected to a large reservoir of a given gas; if one assumes that the large reservoir is well-stirred, thence, the boundary condition for the gas mixture in the tube may be approximated by the known concentration at the reservoir.

For a gas mixture in contact with a condensed phase, the typical boundary conditions for a species concentration, assuming ideal mixtures, is Raoult's law (deduced in [Mixtures](#)):

$$\frac{x_{i,\text{gas}}}{x_{i,\text{condensed}}} = \frac{p_i^*(T)}{p} \xrightarrow{\text{pure condensed phase}} x_{i,\text{vap}} = \frac{p_i^*(T)}{p} = \frac{p_u}{p} \exp\left(A - \frac{B}{C + T/T_u}\right) \quad (7)$$

where [Antoine's fitting coefficients](#) for the vapour pressure curve have been explicitly shown (see [Phase Change](#) for an explanation). Notice that sublimation vapour-pressure data should be used when the source is solid, e.g. when ice is the source of water vapour, instead of liquid water. For instance, the boundary value for water-vapour diffusion in ambient air close to a water pool at 15 °C is $x_{i,\text{vap}}=0.017$, corresponding to the two-phase equilibrium pressure of pure water at 15 °C: 1.7 kPa. When gases are sparingly soluble, Henry's law must be used instead of Raoult's law (see [Solutions](#)).

Exercise 2. Find the concentration of carbon dioxide at a water surface at 25 °C, when exposed to a gas stream with a partial pressure of CO₂ of 300 kPa.

Solution. Henry's law data can be found in a bewildering variety of manners, and with different units, usually under the common name of 'Henry constant', K_H . For solubility of CO₂ in water at 25 °C, we may find, from the solubility data (Table 3) in [Solutions](#), $K_H=c_{i,\text{liq}}/c_{i,\text{gas}}=0.80$, meaning that, for CO₂ to be at equilibrium between the aqueous phase and the gas phase, there must be 0.80 mol/m³ of CO₂ dissolved in water per each 1 mol/m³ of CO₂ dissolved in the gas phase (or pure). We might find the same number but referring to mass concentrations, since they are just proportional with the factor $M_{\text{CO}_2}=0.044$ kg/mol, (3), $K_H=\rho_{i,\text{liq}}/\rho_{i,\text{gas}}=0.80$, meaning that, for CO₂ to be at equilibrium between the aqueous phase and the gas phase, there must be 0.80 kg/m³ of CO₂ dissolved in water per each 1 kg/m³ of CO₂ dissolved in the gas phase (or pure). Those are the only non-dimensional 'constants' (constant in Henry's law, and other equilibrium laws in Chemistry, means that it only depends on temperature, not on pressure).

We might find $K_H=c_{i,liq}/p_{i,gas}=32 \text{ (mol/m}^3\text{)}/\text{bar}$, meaning that, for CO₂ to be at equilibrium between the aqueous phase and the gas phase, there must be 32 mol/m³ of CO₂ dissolved in water per each 1 bar (100 kPa) of partial pressure of CO₂ dissolved in the gas phase (or pure); of course, we can check for consistency: $c_{i,liq}/c_{i,gas}=RTc_{i,liq}/p_{i,gas}$, but it is prone to trivial errors on unit conversion (e.g. the 10⁵ in $c_{i,liq}/c_{i,gas}=RTc_{i,liq}/p_{i,gas}=0.80=8.3\cdot 298\cdot 32/10^5$).

We might find $K_H=x_{i,liq}/p_{i,gas}=580 \text{ ppm_mol}/\text{bar}$, meaning that, for CO₂ to be at equilibrium between the aqueous phase and the gas phase, there must be 580 parts-per-million in molar base of CO₂ dissolved in water per each 1 bar (100 kPa) of partial pressure of CO₂ dissolved in the gas phase (or pure); we can check for consistency: $c_{i,liq}/c_{i,gas}=(\rho_m RT/M_m)x_{i,liq}/p_{i,gas}$, where subindex m referring to the solution, which can be approximated as pure water, and thence $c_{i,liq}/c_{i,gas}=(\rho_m RT/M_m)x_{i,liq}/p_{i,gas}=0.80=(1000\cdot 8.3\cdot 298/0.018)\cdot 580\cdot 10^{-6}/10^5$.

We might find $K_H=c_{i,liq}/c_{i,gas,STP}=0.73 \text{ m}^3\text{(STP)}/\text{bar}$, meaning that, for CO₂ to be at equilibrium between the aqueous phase and the gas phase at 25 °C, the amount of CO₂ dissolved in 1 m³ of solution, per each 1 bar (100 kPa) of partial pressure of CO₂ dissolved in the gas phase (or pure), would occupy 0.73 m³ at STP-conditions of 0 °C and 100 kPa; we can check for consistency: $c_{i,liq}/c_{i,gas,STP}=(c_{i,liq}/c_{i,gas})/(T_{STP}/T^\oplus)=0.80\cdot 273/298=0.73$, where subindex m referring to the solution, which can be approximated as pure water, and thence $c_{i,liq}/c_{i,gas}=(\rho_m RT/M_m)x_{i,liq}/p_{i,gas}=0.80=(1000\cdot 8.3\cdot 298/0.018)\cdot 580\cdot 10^{-6}/10^5$.

In summary, if we assume that pure carbon dioxide at 300 kPa (or a gas mixture with that partial pressure of CO₂) is at equilibrium with water at 25 °C, the CO₂ concentration in the gas phase is $c_{i,gas}=x_i p/(RT)=300\cdot 10^5/(8.3\cdot 298)=121 \text{ mol/m}^3$, and the CO₂ concentration in solution is $c_{i,liq}=K_H c_{i,gas}=0.80\cdot 121=97 \text{ mol/m}^3$, i.e. 0.17% of the molecules in the liquid phase are CO₂, and 99.8% are H₂O molecules (assuming no other solute is present); it can also be concluded that, if all the CO₂ dissolved in 1 m³ of water at equilibrium at 25 °C and 100 kPa, were extracted and put at STP-conditions (0 °C and 100 kPa), it would occupy a volume of 2.2 m³.

For a liquid mixture in contact with another condensed phase (a solid or an immiscible liquid), the boundary condition for a species concentration, i , called a solute, cannot be modelled in a simple form as Raoult's law; at most, in the ideal case, from the equality of the solute chemical potential in both phases one gets:

$$\ln \frac{x_{i,liq}}{x_{i,sol}} = \frac{\mu_{i,sol}(T) - \mu_{i,liq}(T)}{R_u T} = \frac{-\Delta g_{i,sol-liq}(T)}{R_u T} = \frac{-\Delta h_{i,sol-liq}(T)}{R_u T} + \frac{\Delta s_{i,sol-liq}(T)}{R_u} \quad (8)$$

where the other phase has been labelled 'sol' both for the case of a solid or an immiscible liquid. In the case of a pure solid as a source of solute, the boundary condition (8) yields $x_{i,liq}=\exp((\mu_{i,sol}-\mu_{i,liq})/(R_u T))$, and it is known as the solubility of the solid solute in the liquid solvent specified (i.e. the maximum molar fraction of solute the liquid can hold). [Solubility data for solid and liquid solutes in a liquid solvent can be found aside.](#)

Diffusion of species within a solid is much more intricate, particularly when the solid is porous or is in a granular state, where hydrodynamic flow appears (seepage). Diffusion through one-piece solids is nearly negligible in most cases at room temperature, but can be studied with Henry's law (some values are given in [Solutions](#)). Gas solubility in solids increases with temperature, contrary to what happens in liquids, and subsequent degassing on cooling may be a nuisance (may even ruin a casting process by creating porosity and voids). Besides, chemical reactions may occur at room temperature (e.g. oxidation) but particularly when the temperature is increased to enhance mass transfer.

SPECIES BALANCE EQUATION

For a given species i in a mixture (solid, liquid or gaseous), its mass balance for a control volume is (accumulation = flux + production):

$$\frac{dm_i}{dt} = \sum_{surfaces} \dot{m}_i + \dot{m}_{i,gen} = -\int_A \vec{j}_i \cdot \vec{n} dA + \int_V w_i dV \quad (9)$$

where m_i is the mass of species i in the volume V , \vec{j}_i is the local mass-flux of species i at the surface area A , and w_i a possible local species generation density due to chemical reactions. For a control-volume system of differential volume $dx dy dz$, with the continuum model:

$$\begin{aligned} \frac{\partial \rho_i}{\partial t} dx dy dz &= \left[\rho_i v_{ix} dy dz - \left(\rho_i v_{ix} + \frac{\partial(\rho_i v_{ix})}{\partial x} dx \right) dy dz + \rho_i v_{iy} dz dx - \left(\rho_i v_{iy} + \frac{\partial(\rho_i v_{iy})}{\partial y} dy \right) dz dx + \dots \right] + w_i dx dy dz \\ \longrightarrow \frac{\partial \rho_i}{\partial t} + \nabla \cdot (\rho_i \vec{v}_i) &= w_i \end{aligned} \quad (10)$$

where ρ_i is its mass density and \vec{v}_i the local velocity of the i -component fluid in a fix reference frame. For a one-component fluid, the mass balance (10) reduces to $\partial \rho / \partial t + \nabla \cdot (\rho \vec{v}) = 0$, the well-known continuity equation of Fluid Mechanics, that can be recovered by summation in (10) for all the species i in the mixture; i.e.:

$$\frac{\partial \sum \rho_i}{\partial t} + \nabla \cdot \sum (\rho_i \vec{v}_i) = \sum w_i \xrightarrow{\text{with } \vec{v} = \sum (\rho_i \vec{v}_i) / \rho} \frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \vec{v}) = 0 \quad (11)$$

Notice that a similar argument might have been followed with molar densities instead of mass densities, and a molar-averaged velocity defined that would not coincide in general with the mass-averaged velocity \vec{v} , that is traditionally used.

Besides the species balance in a generic differential volume (10), the species balance in a generic interface must be established in many problems:

$$0 = \dot{m}_{i,out} - \dot{m}_{i,in} + \dot{m}_{i,surface-gen} \quad (12)$$

where the last term, species generation at the interface, only appears in the case of heterogeneous reactions at the interface.

Diffusion rate: Fick's law

Actual mixing of chemical species is governed by mass-transfer laws very similar to heat-transfer laws, establishing a linear proportion between forces and fluxes: in Heat Transfer, a linear proportion between the temperature-gradient, and the energy flow as heat; in Mass Transfer, a linear proportion between the species density-gradient, and the relative velocity of the species-fluid to the mean-fluid. The basic kinetic-law for mass diffusion was proposed in 1855 by the German physiologist A. Fick for a homogeneous media without phase changes or chemical reactions, namely:

$$\frac{\dot{m}_{di}}{A} \vec{n} = \rho_i (\vec{v}_i - \vec{v}) \equiv \rho_i \vec{v}_{di} \equiv \vec{j}_{di} = -D_i \nabla \rho_i, \quad \text{with} \quad \vec{j}_i = y_i \vec{j} + \vec{j}_{di} \quad (13)$$

that reads: the mass-flow-rate of species i diffusing per unit area in the normal direction \vec{n} (mass-diffusion flux of species i), \vec{j}_{di} , which is its density times the relative velocity of the species-fluid to the mean-fluid (the latter difference simply called diffusion speed $\vec{v}_{di} \equiv \vec{v}_i - \vec{v}$), is proportional and opposes to the species density-gradient, $\nabla \rho_i$, with the proportionality constant D_i named mass-diffusivity for species i in the given mixture, and $\rho_i = y_i \rho$ the mass-density for species i in the given mixture. Notice that Fick's law, $\vec{j}_{di} = -D_i \nabla \rho_i$, only accounts for mass-flow-rates and fluxes due to diffusion (by a gradient in concentration); if there is a convective flux $\vec{j} \equiv \rho \vec{v}$ (not associated to gradients in concentration but to bulk transport at speed \vec{v}), then the net flux of species i is $\vec{j}_i = y_i \vec{j} + \vec{j}_{di}$, or $\rho_i \vec{v}_i = \rho_i \vec{v} + \rho_i \vec{v}_{di}$, which was used in (13).

The original Fick's law (13), which he proposed just emulating Fourier's law (of 1822), perfectly matches experiments with dilute solutions, i.e. when the properties of the medium can be assumed independent of the species i concentration, and (13) can also be written as $\vec{j}_i = -\rho D_i \nabla y_i$, the most general Fick's law statement, extending (13) to cover diffusion at high concentrations. Even in the original case he tried, salt diffusion along a test tube from a saturated brine below to a fresh-water-swept zero-concentration at the mouth, with a density jump from 1200 kg/m³ at the salt-brine interface and 1000 kg/m³ at the top surface, deviations from the linear density profile corresponding to the one-dimensional steady-state problem with constant D_i are less than a 1% at most; he found $D_{\text{salt,water}} = 0.12 \cdot 10^{-9} \text{ m}^2/\text{s}$.

Fick's law is similar to Fourier's law for heat transfer $\vec{q} = -k \nabla T$ (or $\vec{q} = -a \nabla (\rho c_p T)$ for a constant-property medium), and applies to gases, liquids and solid mixtures, with D_i depending on the diffusing species i , the medium and its thermodynamic state. Fick's law is also similar to Darcy's law of mean fluid velocity through porous-media $\vec{v} = -\kappa \nabla (h + p/(\rho g))$, and to Newton's law of momentum transport by viscosity $\vec{\tau} = -\nu \nabla (\rho \vec{v})$ for a constant-density fluid of kinematic viscosity ν , where $\vec{\tau}$ is the stress tensor. In fact, for gases, a simplified analysis dictates that $D_i = \alpha = \nu$.

Notice that only the flux associated to the main driving force is considered in Eq. (13), i.e. mass-diffusion due to a species-concentration gradient (as for heat-diffusion due to a temperature gradient). There are

also secondary fluxes associated to other possible gradients (e.g. mass-diffusion due to a temperature gradient, known as Soret effect, and mass-diffusion due to a pressure gradient; alternatively, there may be heat-diffusion due to a species-concentration gradient, known as Dufour effect, and heat-diffusion due to a pressure gradient), but most of the times those cross-coupling fluxes are negligible. Besides, selective force fields may yield diffusion (e.g. ions in an electric field). Typical values for D_i (and the thermal diffusivity $a=k/(\rho c_p)$) are given in Table 1, with Schmidt numbers, $Sc=v/D_i$, to evaluate non-ideality in gases (kinetic theory of ideal gases predicts $Sc=1$); for air solutions, the dynamic viscosity is practically that of air, $\nu=15.9 \cdot 10^{-6} \text{ m}^2/\text{s}$ at 300 K. for aqueous solutions, the dynamic viscosity is practically that of water, $\nu=0.86 \cdot 10^{-6} \text{ m}^2/\text{s}$ at 300 K.

Table 1. Typical values for mass and thermal diffusivities, D_i and a , and Schmith number, Sc , all at 300 K (extracted from [Mass diffusivity data](#)).

Substance	Diffusivity	Typical values	Example	$Sc=v/D_i$
Gases ^{a)}	a	$10^{-5} \text{ m}^2/\text{s}$	$a_{\text{air}}=22 \cdot 10^{-6} \text{ m}^2/\text{s}$	
			$a_{\text{CH}_4}=24 \cdot 10^{-6} \text{ m}^2/\text{s}$	
	D_i	$10^{-5} \text{ m}^2/\text{s}$	$D_{\text{waterapour,air}}=24 \cdot 10^{-6} \text{ m}^2/\text{s}$	0.66
			$D_{\text{CO}_2,\text{air}}=14 \cdot 10^{-6} \text{ m}^2/\text{s}$ ($390 \cdot 10^{-6} \text{ m}^2/\text{s}$ at 2000 K)	1.14
			$D_{\text{CH}_4,\text{air}}=16 \cdot 10^{-6} \text{ m}^2/\text{s}$	0.99
Liquids ^{b)}	a	$10^{-7} \text{ m}^2/\text{s}$	$a_{\text{water}}=0.16 \cdot 10^{-6} \text{ m}^2/\text{s}$	
	D_i	$10^{-9} \text{ m}^2/\text{s}$	$D_{\text{N}_2,\text{water}}=3.6 \cdot 10^{-9} \text{ m}^2/\text{s}$	240
			$D_{\text{O}_2,\text{water}}=2.5 \cdot 10^{-9} \text{ m}^2/\text{s}$	340
Solids ^{c)}	a	$10^{-6} \text{ m}^2/\text{s}$	$a_{\text{steel}}=13 \cdot 10^{-6} \text{ m}^2/\text{s}$	
			$a_{\text{ice}}=1.3 \cdot 10^{-6} \text{ m}^2/\text{s}$	
			$a_{\text{fresh food}}=0.13 \cdot 10^{-6} \text{ m}^2/\text{s}$	
	D_i	$10^{-12} \text{ m}^2/\text{s}$	$D_{\text{N}_2,\text{rubber}}=150 \cdot 10^{-12} \text{ m}^2/\text{s}$	
			$D_{\text{H}_2,\text{polyethylene}}=87000 \cdot 10^{-12} \text{ m}^2/\text{s}$	
			$D_{\text{H}_2,\text{steel}}=0.3 \cdot 10^{-12} \text{ m}^2/\text{s}$	

a) For gas diffusion, both for a and D_i , a general dependence with temperature and pressure of the form T^n/p can be used, with $1.5 < n < 2$ (according to simple kinetic gas theory, $n=3/2$).

b) Mass diffusion in liquids grows with temperature, roughly inversely proportional viscosity-variation with temperature.

c) Mass diffusion in solids is often not well represented by Fick's law, so that diffusion coefficients might not be well-defined, and other (empirical) correlations are applied instead of Fick's law.

Notice that the definition of Fick's law in (13) has been established in mass terms, but an analogous development could have been made in molar terms:

$$\frac{\dot{n}_{di}}{A} \vec{n} = c_i (\vec{v}_i - \vec{v}) \equiv c_i \vec{v}_{di} \equiv \vec{J}_{di,molar} = -D_i \nabla c_i \quad (14)$$

Finally, notice that all the above expressions of Fick's law (13-14) assume a constant density medium, and will give good predictions for diffusion in dilute mixtures, e.g. when $x_i < 0.1$ all around ($x_{i,max}=0.104$ in Fick's original experiment). But what happens in mixtures with large density gradients like the diffusion

through a tube connecting two large reservoirs of hydrogen and nitrogen (or air) where $x_i=0$ at one end and $x_i=1$ at the other? As said above, the real driving force for mass diffusion is not ∇c_i as in (14) neither $\nabla \rho_i$ as in (13), but $\nabla \mu_i$. The only explicit relation between concentration variables and the chemical potential corresponds to ideal mixtures, where $\nabla \mu_i = R_u T \nabla \ln x_i$. Even if we assume for simplicity that the flux is proportional to ∇x_i (and not to $\nabla \ln x_i$), i.e. $\vec{j}_{d1} = -K_{12} \nabla x_1$ with K_{12} independent of x_1 , the following identity applies for a non-diluted binary mixture:

$$\vec{j}_{d1} = -K_{12} \nabla x_1 = -K_{12} \nabla \frac{\frac{y_1}{M_1}}{\frac{1}{M_m(z)}} = -K_{12} \frac{M_m(z)}{M_2} \nabla y_1 = -\rho_m(z) D_{12} \nabla y_1 \quad (15)$$

showing that the assumption of K_{12} independent of z is still equivalent to the assumption of D_{12} independent of z only for gaseous non-diluted mixtures, where the variation of mixture density along the length, $\rho_m(z)$, compensates with the variation of mixture molar-mass, $M_m(z)$. Thence, we may use $\vec{j}_{d1} = -\rho_m(z) D_{12} \nabla y_1$ for dilute mixtures in any physical state (solid, liquid or gas), and for non-dilute mixtures in the gaseous state.

The binary diffusion model just described (one species diffusing in an independent medium) requires some averaging when several species diffuse in a medium, as for exhaust gases in ambient air; in some cases, considering an equivalent global diffusing species of molar fraction $x_{i,\text{global}} = \sum x_i$ and an equivalent average diffusivity $D_{i,\text{avrg}}$ given by $x_{i,\text{global}}/D_{i,\text{avrg}} = \sum (x_i/D_i)$, has given good results.

Exercise 3. Find the species diffusion speed in the complete combustion of solid carbon in air at 300 K and 100 kPa, knowing that the reaction $\text{C} + \text{O}_2 = \text{CO}_2$ takes place at the surface, which attains 1500 K, consuming 2.2 grams of carbon per second, per square meter, and that mass fractions in the gas close to the surface are $y_{\text{N}_2} = 0.75$, $y_{\text{O}_2} = 0.15$, and $y_{\text{CO}_2} = 0.10$.

Solution. The aim of this exercise is to make clear some common misconceptions, as thinking that, because 1 mol of gas is released by each mol of oxidiser consumed, there would be no macroscopic velocities but just diffusion.

We only deal here with the mass transfer process, and only partially, since we do not compute the composition at the surface (we assume we know them), what really comes from a combined heat and mass transfer interaction, as well as the 1500 K at the surface. We only work here with fluxes, i.e. flow-rates per unit area, since we keep close to the surface, although the real problem may correspond to the burning of a carbon slab or of a small quasi-spherical carbon particle. Of course, the data would be constant in the ideal planar case, but may change with time for other geometries.

The applicable equations are (9-15). Let us start with the fuel flow-rate. The supplied data is the carbon flux $j_c \equiv \dot{m}_c / A = 0.0022 \text{ (kg/s)/m}^2$, which can be interpreted as a consumption of carbon in the real unsteady process for a fixed control volume (fixed reference frame), or as a steady sink of carbon at the combustion front in the quasi-steady process for a thin control volume centred at the surface and moving with it at the receding speed (moving reference

frame); the latter can also be thought of as a source of carbon in an imaginary strictly-steady process in which the front does not move because new fuel is injected into the system (that can now be either of interfacial or volumetric size). In the fix-frame case, there is no velocities within the fuel (it is only de interface that is receding), whereas in the moving-frame case the fuel has a positive speed $v_C = j_C / \rho_C = 0.0022 / 2200 = 1.0 \cdot 10^{-6}$ m/s, having placed the combustion front at the origin, the fuel to the left-hand-side of the front, and taking the density of carbon 2200 kg/m^3 from [Solid data tables](#).

In moving axes, the stoichiometry $C + O_2 = CO_2$ indicates that the required flux of oxygen is the same in molar basis, or, in mass terms $j_{O_2} = -j_C M_{O_2} / M_C = -0.0022 \cdot 0.032 / 0.012 = -0.0059 \text{ kg/(s}\cdot\text{m}^3)$, where the minus sign takes account of the direction of the oxygen flow (from the air at right to the front at the origin). Similarly, $j_{CO_2} = j_C M_{CO_2} / M_C = 0.0022 \cdot 0.044 / 0.012 = 0.0081 \text{ kg/(s}\cdot\text{m}^3)$; of course, a global mass balance dictates that $|j_C| + |j_{O_2}| = |j_{CO_2}|$ (here $0.0022 + 0.0059 = 0.0081$; notice the extreme care needed to deal with the sign of fluxes, which are positive in the geometrical sense if they point to the right, but positive in the thermodynamic sense if they enter the system). Nitrogen has no net bulk motion and thus $j_{N_2} = 0$. Notice that $y_{N_2} + y_{CO_2} + y_{O_2} = 1$ at every stage in the gas phase, where $y_C = 0$.

But the original question was on diffusion speeds. First of all, we must realise that all the above fluxes are net fluxes in the moving frame, not diffusion or convection fluxes. The global convection flux is obtained by averaging net fluxes for all species at a point, $j = \sum j_i$. Thence, on the left of the front, where there is only pure fuel (solid carbon) the convective flux coincides with the net flux, and there is no diffusion, $j = \sum j_i = j_C = 0.0022 \text{ kg/(s}\cdot\text{m}^3)$. On the right side of the front, the sum of fluxes is (there is no fuel) $j = \sum j_i = j_{O_2} + j_{CO_2} + j_{N_2} = -0.0059 + 0.0081 + 0 = 0.0022 \text{ kg/(s}\cdot\text{m}^3)$, as can be expected from the global mass balance in moving axes ($0.0022 \text{ kg/(s}\cdot\text{m}^3)$ enter the front and $0.0022 \text{ kg/(s}\cdot\text{m}^3)$ exit it). We conclude then that the diffusion fluxes are $j_{di} = j_i - y_i \sum j_i$; $j_{d,O_2} = j_{O_2} - y_{O_2} \sum j_i = -0.0059 - 0.15 \cdot 0.0022 = -0.0062 \text{ kg/(s}\cdot\text{m}^3)$, $j_{d,CO_2} = j_{CO_2} - y_{CO_2} \sum j_i = 0.0081 - 0.10 \cdot 0.0022 = 0.0079 \text{ kg/(s}\cdot\text{m}^3)$, and $j_{d,N_2} = j_{N_2} - y_{N_2} \sum j_i = 0 - 0.75 \cdot 0.0022 = -0.0017 \text{ kg/(s}\cdot\text{m}^3)$.

We finally get from (13) the diffusion speeds sought, $j_{di} = \rho_i v_{di}$, with $\rho_i = y_i \rho$ and $\rho = p / (RT) = 10^5 / (287 \cdot 1500) = 0.23 \text{ kg/m}^3$ with the ideal gas model and the gas constant for standard air (we can compute the molar mass of the mixture, since we know the composition, but the effect is minimal since nitrogen is always dominant). Thence, the diffusion speeds are $v_{d,O_2} = j_{d,O_2} / (y_{O_2} \rho) = -0.0062 / (0.15 \cdot 0.23) = -0.18 \text{ m/s}$ and $v_{d,CO_2} = j_{d,CO_2} / (y_{CO_2} \rho) = 0.0079 / (0.10 \cdot 0.23) = 0.34 \text{ m/s}$, and $v_{d,N_2} = j_{d,N_2} / (y_{N_2} \rho) = -0.0017 / (0.75 \cdot 0.23) = -0.0096 \text{ m/s}$. The latter result is worth analysing: is then nitrogen diffusing, being an inert component in this combustion process? Yes, nitrogen diffuses towards the combustion front (were its concentration is smaller), to compensate the carry-over by the global convecting flow.

Notice that there is an overall convection speed $v = \sum j_i / \rho = 0.0022 / 0.23 = 0.0096 \text{ m/s}$ (i.e. to the right), so that the 'absolute' speeds (still in the moving frame) for each species are $v_{O_2} = v + v_{d,O_2} = 0.0096 - 0.18 = -0.17 \text{ m/s}$, $v_{CO_2} = v + v_{d,CO_2} = 0.0096 + 0.34 = 0.35 \text{ m/s}$, and $v_{N_2} = v + v_{d,N_2} = 0.0096 - 0.0096 = 0$. Besides, in the fixed frame, the moving frame has a receding

speed opposite the fuel-feeding speed above computed, $v_c = j_c / \rho_c = 0.0022 / 2200 = 1.0 \cdot 10^{-6}$ m/s, which is insignificant to the others.

THE DIFFUSION EQUATION FOR MASS TRANSFER

The substitution of Fick's law (13) in the species mass balance (10), and the assumption of constant diffusivity, gives the mass-diffusion equation:

$$\frac{\partial \rho_i}{\partial t} + \nabla \cdot (\rho_i \vec{v} + \rho_i \vec{v}_{di}) = w_i \longrightarrow \frac{\partial \rho_i}{\partial t} + \nabla \cdot (\rho_i \vec{v}) - D_i \nabla^2 \rho_i = w_i \quad (16)$$

entirely similar to the heat equation, that is here presented together to better grasp their similarity. For a unit-control-volume system, the species balance (in terms of mass fractions $y_i = \rho_i / \rho$) and the heat balance (in terms of temperature), adopt the following form:

Balance of	Accumulation	=	Production	Diffusive flux	Convective flux	
mass of species i	$\frac{\partial y_i}{\partial t}$	=	$\frac{w_i}{\rho}$	$+ D_i \nabla^2 y_i$	$- \nabla \cdot (y_i \vec{v})$	(17)
thermal energy	$\frac{\partial T}{\partial t}$	=	$\frac{\phi}{\rho c_p}$	$+ a \nabla^2 T$	$- \nabla \cdot (T \vec{v})$	(18)

where, again, w_i is mass-production rate per unit volume by chemical reaction, ϕ is heat-production rate per unit volume (e.g. by internal energy dissipation or external energy deposition), D_i is species diffusivity, and $a = k / (\rho c_p)$ thermal diffusivity. The constancy of overall density, $\rho = \text{constant}$, has been introduced to pass from (16) to (17), a good approximation for dilute mixtures. Notice that with this approximation the continuity equation reduces to $\nabla \cdot \vec{v} = 0$. Another useful form of the mass and energy balances is obtained using the convective derivative $D() / Dt \equiv \partial() / \partial t + \vec{v} \cdot \nabla()$:

$$\frac{Dy_i}{Dt} = D_i \nabla^2 y_i + \frac{w_i}{\rho} \Leftrightarrow \frac{D\rho_i}{Dt} = D_i \nabla^2 \rho_i + w_i \Leftrightarrow \frac{Dc_i}{Dt} = D_i \nabla^2 c_i + \frac{w_i}{M_i} \Leftrightarrow \frac{Dx_i}{Dt} = D_i \nabla^2 x_i + \frac{Mw_i}{M_i \rho} \quad (19)$$

similarly to the heat equation:

$$\frac{DT}{Dt} = a \nabla^2 T + \frac{\phi}{\rho c} \quad (20)$$

The diffusion equation, (20) or (19), is a second order parabolic partial differential equation (PDE), to be solved with the particular boundary and initial conditions of the problem at hand. There are only a few cases where analytical solutions can be found, mostly for problems with very simple geometry (e.g. unbounded conditions) in steady state, or when the unsteady state has a self-similar solution reducing the diffusion equation to an ordinary differential equation (ODE), as presented in [Heat conduction](#). Otherwise, i.e. in most practical problems, the diffusion equation has to be solved numerically (usually by finite-element or finite-difference methods), as presented in [Heat conduction](#) too.

Notice also that, for linear equations, the superposition principle applies and a series of solutions can be assembled to meet particular boundary conditions.

SOME ANALYTICAL SOLUTIONS TO MASS DIFFUSION

Although solutions to the mass diffusion equation are similar to those of the heat equation, we give here some particular applications of mass diffusion, as an example of how easy it is to convert from one formulation to the other.

As any other time-dependant multi-dimensional phenomena, mass-diffusion models may be classified according to their dimensionality: steady, 1D problems (planar, cylindrical or spherical), 2D problems and 3D problems. We start by considering one of the simplest cases, the instantaneous point-source deposition, a key problem in mass transfer (as the instantaneous point-source release in heat conduction).

Instantaneous point-source

Consider the self-similar diffusion, in time and space, which can be planar, cylindrical or spherical, of a pulse deposition of a finite amount of mass, m_i of species i , in an unbound non-moving medium of different composition; i.e. if at time $t < 0$ there were no species i , and at time $t = 0$ a finite amount m_i is deposited at $r = 0$; how will it diffuse for $t > 0$? The solution is the principal solution (i.e. a point-source in an unbound medium) of the diffusion equation, which, in terms of the mass-density of species i , $\rho_i \equiv m_i/m$, is:

$$\frac{\partial \rho_i}{\partial t} = D_i \frac{1}{r^n} \frac{\partial}{\partial r} \left(r^n \frac{\partial \rho_i}{\partial r} \right) \rightarrow \rho_i(r, t) = \frac{m_i \exp\left(\frac{-r^2}{4D_i t}\right)}{(4\pi D_i t)^{\frac{1+n}{2}}} \quad (21)$$

with $n=0$ for the planar case (m_i is then the mass released per unit interface area), $n=1$ for cylindrical case (m_i is then mass released per unit axial length), and $n=2$ for the spherical case. This point-source solution is plotted in Fig. 1 for three time instants, and has the following properties:

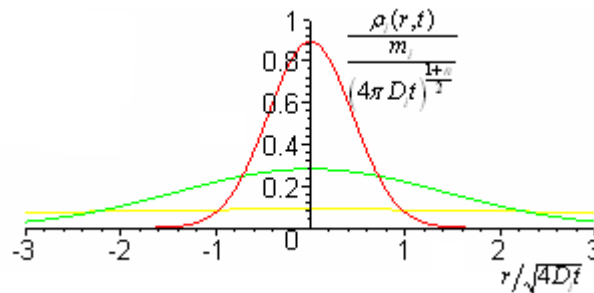


Fig. 1. Point-source diffusion. Species distribution at three time instants.

- It is only valid for $t > 0$, where it is a Gauss-bell shape (it is a Dirac delta function at $t = 0$, and does not exist for $t < 0$).
- The mass of the species diffusing is conserved:

$$\text{for } n=0 \int_{-\infty}^{\infty} \rho_i(r, t) dr = m_i, \quad \text{for } n=1 \int_0^{\infty} \rho_i(r, t) 2\pi r dr = m_i, \quad \text{for } n=2 \int_0^{\infty} \rho_i(r, t) 4\pi r^2 dr = m_i \quad (22)$$

- The maximum density occurs at the origin and decays with time as:

$$\rho_i(0,t) = \frac{m_i}{(4\pi D_i t)^{\frac{1+n}{2}}} \quad (23)$$

i.e. as $1/t^{1/2}$ in the planar case, as $1/t$ in the cylindrical case, and as $1/t^{3/2}$ in the spherical case. Of course, the model cannot be valid for very short times; the density of species i cannot be larger than in its pure state (e.g. its liquid density for a drop diffusing in a liquid media, or its gas density for a puff diffusing in a gas media).

Semi-infinite planar diffusion

Another key problem is the inter-diffusion when two quiescent semi-infinite media (e.g. two different gases) are brought into contact, either by removal of a separating wall, or by parallel injection at the same speed at the end of a semi-infinite wall, what is the same if we change the reference frame, as sketched in Fig. 2.

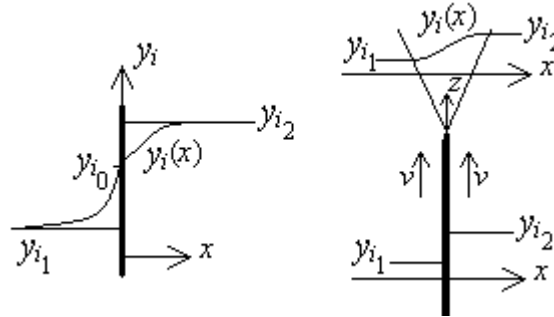


Fig. 2. One-dimensional, planar inter-diffusion: a) initial and generic mass fraction in two quiescent media, b) mass fraction in two media moving at the same speed, before mixing, and while being mixed..

As there is no characteristic length (the two media being semi-infinite), there is a self-similar solution in the combined variable $x/(2(D_i t)^{1/2})$, which, in terms of the mass fraction of species i , y_i , takes the form:

$$\frac{\partial y_i}{\partial t} = D_i \frac{\partial^2 y_i}{\partial x^2} \xrightarrow{\eta = \frac{x}{2\sqrt{D_i t}}} \frac{\partial^2 y_i}{\partial \eta^2} + 2\eta \frac{\partial y_i}{\partial \eta} = 0 \rightarrow y_i = A + B \operatorname{erf}\left(\frac{x}{2\sqrt{D_i t}}\right) \quad (24)$$

to be applied to each of the media by imposing the particular initial and boundary conditions. With subscript '-' for the left-hand-side medium and '+' for the right one, one gets:

$$y_{i-}(x) = A_1 + B_1 \operatorname{erf}\left(\frac{x}{2\sqrt{D_{i1} t}}\right) \begin{cases} y_{i-}(-\infty) = y_{i,1} \longrightarrow A_1 - B_1 = y_{i,1} \\ y_{i-}(0) = y_{i,0} \longrightarrow A_1 = y_{i,0} \\ j_{i,0} = -\rho_1 D_{i1} B_1 \frac{1}{2\sqrt{D_{i1} t}} \end{cases}$$

$$y_{i+}(x) = A_2 + B_2 \operatorname{erf}\left(\frac{x}{2\sqrt{D_{i2}t}}\right) \begin{cases} y_{i+}(\infty) = y_{i,2} \longrightarrow A_2 + B_2 = y_{i,2} \\ y_{i+}(0) = y_{i,0} \longrightarrow A_2 = y_{i,0} \\ j_{i,0} = -\rho_2 D_{i2} B_2 \frac{1}{2\sqrt{D_{i2}t}} \end{cases} \quad (25)$$

what allows finding the six unknowns ($A_1, B_1, A_2, B_2, y_{i,0}, j_{i,0}$) from the six equations, in terms of the data ($y_{i,1}, y_{i,2}$). Of great importance is the value of mass-fraction at the contact, $y_{i,0}$, which happens to be invariant with time, and results in:

$$y_{i,0} = \frac{\rho_1 \sqrt{D_{i1}} y_{i,1} + \rho_2 \sqrt{D_{i2}} y_{i,2}}{\rho_1 \sqrt{D_{i1}} + \rho_2 \sqrt{D_{i2} k_2}} \quad (26)$$

Several other diffusion solutions are presented in Table 2, both in terms of species variables y_i and D_i , and in terms of thermal variables T and a , or just using the latter for ease of writing (to be applied to species-diffusion problem by changing T to y_i , a to D_i , and $Q/(\rho c)$ to m_i).

Exercise 4. A mild steel with $y_C=0.2\%$ (0.2% carbon percent in weight) is to be surface-hardened by exposure to a carbonaceous atmosphere at 1000 K. Assuming an equilibrium concentration of $y_C=1\%$ at that temperature (from solubility data for that carbonaceous mixture conditions), find the required exposure time to achieve $y_C>0.8\%$ at a depth of 1 mm from the surface.

Solution. From Table 1 we get the diffusion coefficient for carbon in iron, $D_{C,iron}=30 \cdot 10^{-12} \text{ m}^2/\text{s}$ at 1000 K. The diffusion equation (24), with the boundary conditions $y_C(0)=y_{C,0}=1\%$, $y_C(\infty)=y_{C,\infty}=0.2\%$, becomes $y_C(x,t)=y_{C,0}-(y_{C,0}-y_{C,\infty})\exp(x/(4D_i t)^{1/2})$, which yields $t=4300 \text{ s}$ (1.2 h) for $y_C=0.8\%$, $y_{C,0}=1\%$, $y_{C,\infty}=0.2\%$, $D_{C,iron}=30 \cdot 10^{-12} \text{ m}^2/\text{s}$, and $x=10^{-3} \text{ m}$. Notice that the assumption of equilibrium at the surface is acceptable because diffusion in the gas phase is much more efficient than in the solid phase.

Diffusion through a wall

We present now a final example of mass diffusion, namely, the simple problem of steady leakage of a gas through a wall, mainly aiming at insisting on the fact that what drives mass diffusion is chemical potential and not concentration, as explained in [Entropy](#).

Exercise 5. Consider gas diffusion through the rubber wall of a nitrogen-filled balloon in air. Assume pure N_2 inside, a 0.01 mm thick rubber wall of 0.5 m in diameter (i.e. a rubber mass of 0.0087 kg), and 300 K and 100 kPa both outside and inside (negligible elastic force). Make a sketch of the nitrogen concentration everywhere, and estimate the relaxation time (e.g. the time for the gradients to dump half-way to equilibrium).

Solution. First of all, notice that we focus just on nitrogen diffusion, but, contrary to heat diffusion where there is only one variable diffusing (thermal energy), here there is nitrogen diffusing outwards to the ambient but at the same time oxygen diffusing inwards.

A second comparison with heat transfer is that mass diffusion through solids is much less efficient than heat diffusion: for a typical elastomer, with data from Solids data, thermal diffusivity is $a \equiv k/(\rho c) = 0.1/(1100 \cdot 2000) = 45 \cdot 10^{-9} \text{ m}^2/\text{s}$, whereas diffusivity for nitrogen in rubber is $150 \cdot 10^{-12} \text{ m}^2/\text{s}$, and for oxygen in rubber $210 \cdot 10^{-12} \text{ m}^2/\text{s}$. This reason alone would explain why for most practical problems solids can be considered impermeable to fluids (i.e. "containers"), but there is more on that.

In fact, the most radical difference between heat diffusion and species diffusion is the abrupt jump on species concentration through an interface, contrary to the continuity of the temperature field. In effect, full thermodynamic equilibrium imposes uniform temperature, uniform velocity, and uniform chemical potential of each species across the interface, but this does not imply uniform species concentration except for uniform phases; at a phase-change interface, equality of chemical potential gives way to a jump in concentration that depends on the materials properties, with two important ideal cases deduced under [Mixtures](#): Raoult's law for the equilibrium of an ideal mixture of gases with an ideal condensed phase, and Henry's law for the equilibrium of an ideal mixture of gases with an ideal dilute condensed phase. The latter is the case here, where a solute (N_2 and O_2) diffuses through a diluted condensed phase (basically rubber macromolecules with very little N_2 and O_2). From the solubility data (Table 3) in [Solutions](#), we can get the Henry constants: $K_{\text{H,N}} = c_{i,\text{sol}}/c_{i,\text{gas}} = 0.04$ for the solubility of nitrogen in rubber at 298 K, and $K_{\text{H,O}} = c_{i,\text{sol}}/c_{i,\text{gas}} = 0.08$ for the solubility of oxygen. You might have noticed that, unfortunately, there is a huge variety on Henry's law data presentation; the one used here was advocated by Ostwald, and means for instance that, for nitrogen to be at equilibrium between both phases, there must be 0.04 mol/m^3 of nitrogen dissolved in rubber per each 1 mol/m^3 of nitrogen dissolved in the gas phase. Notice, by the way, that all interfaces are selective to some extent (e.g. rubber lets oxygen to flow more readily than nitrogen), what can be advantageously used for separation of species from a mixture.

In our case, inside the balloon, nitrogen is pure, with a concentration of $c = p/(RT) = 10^5/(8.3 \cdot 300) = 40 \text{ mol/m}^3$ of nitrogen, whereas in the air outside there is a concentration of $c_{\text{N}} = x_{\text{N}}p/(RT) = 0.79 \cdot 10^5/(8.3 \cdot 300) = 32 \text{ mol/m}^3$ of nitrogen. We can assume that these equilibrium concentrations apply also close to the rubber even during non-equilibrium (i.e. while diffusion is taking place), due to the small fluxes implied.

Within the balloon matter itself, the equilibrium concentrations at each end are the following. At the internal interface, $c_{\text{N,sol}} = K_{\text{H,N}}c_{i,\text{gas}} = 0.04 \cdot 40 = 1.6 \text{ mol/m}^3$ of nitrogen, whereas at the external interface, $c_{\text{N,sol}} = K_{\text{H,N}}c_{i,\text{gas}} = 0.04 \cdot 32 = 1.3 \text{ mol/m}^3$ of nitrogen. What results in the concentration profile shown in Fig. 3a.

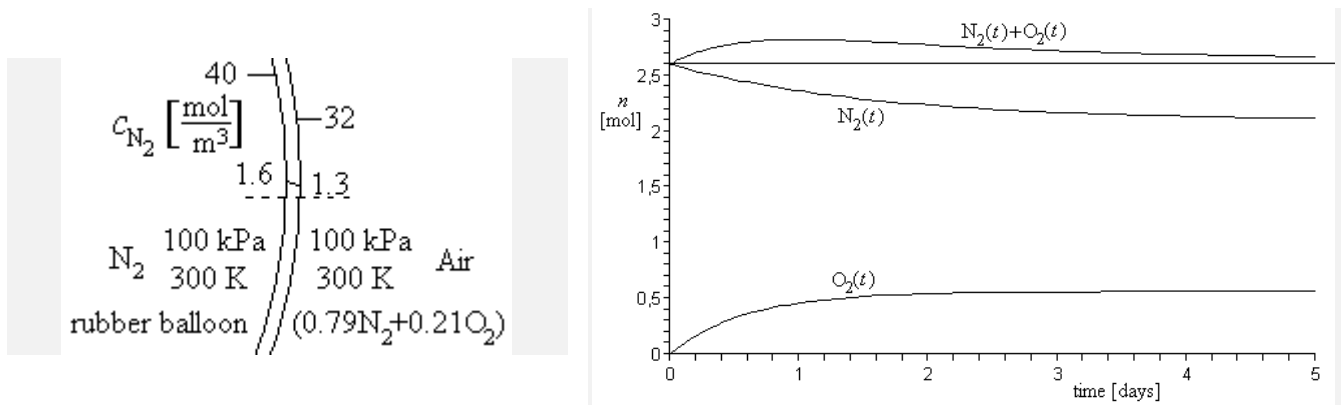


Fig. 3. Gas diffusion through a rubber wall: a) Initial concentration profile for nitrogen diffusion from a nitrogen-filled balloon (left) to ambient air (right); notice that nitrogen diffuses against the concentration jump in the outer interface. b) Time evolution of the amounts of nitrogen, oxygen, and the sum, inside the balloon.

Finally, for the estimation of the relaxation time, we must compute the mass-diffusion flux $j_N = -D_{i,N} \nabla \rho_N$, (13), or in molar terms, (14), $j_{N,\text{molar}} = -D_{i,N} \nabla c_N = -D_{i,N} (c_{N,\text{ext}} - c_{N,\text{int}}) / L_{\text{th}} = -150 \cdot 10^{-12} (1.3 - 1.6) / 10^{-5} = 5 \cdot 10^{-6}$ (mol/s)/m² of nitrogen. With a balloon area of $A = \pi D^2 = 0.79$ m² ($V = \pi D^3 / 6 = 0.065$ m³), and an initial content of $n_N = pV / (RT) = 10^5 \cdot 0.065 / (8.3 \cdot 300) = 2.6$ mol, we have a rough estimate $t_{\text{half}} = n_N / (j_{N,\text{molar}} \cdot A) = 2.6 / (5 \cdot 10^{-6} \cdot 0.79) = 0.7 \cdot 10^6$ s, i.e. of the order of 8 days (no wonder why one always starts neglecting diffusion through solids). But this analysis is too crude: what happens to internal pressure, or balloon volume, when nitrogen disappears? What about the oxygen flux? The latter is $j_{O,\text{molar}} = -D_{i,O} \nabla c_O = -D_{i,O} (c_{O,\text{ext}} - c_{O,\text{int}}) / L_{\text{th}} = -210 \cdot 10^{-12} (0 - 0.67) / 10^{-5} = -14 \cdot 10^{-6}$ (mol/s)/m² of oxygen. You can observe that oxygen flux is three times that of nitrogen, what might have been expected from the higher solubility of oxygen in rubber, and the higher diffusivity, the jump in concentration being equal (from 40 mol/m³ to 32 mol/m³ for nitrogen, and from 0 to 8 mol/m³ for oxygen; the sum being 40 mol/m³ in each side as expected for ideal gases at the same temperature and pressure). So, what happens to internal pressure and volume? It depends on the elastic law for the rubber.

In any case, the equation $pV = nRT$ shows that, at $T = \text{constant}$ (very slow process) and with n initially increasing because the inflow of O₂ is larger than the outflow of N₂, the product pV should increase initially but decrease afterwards because final equilibrium must be with the same composition everywhere, and thus recovering the same initial pV -values. The maximum can be found to be 8% larger than initial conditions ($pV_{\text{max}} = 1.08 pV_{\text{ini}}$), and to take place about one day from the beginning, as shown in Fig. 3b.

Summary table of analytical solutions to diffusion problems

Table 2. Analytical solutions to some diffusion problems.

Problem	Sketch	Solution	Notes
Instantaneous point-source deposition, one-, two-, tri-dimensional		$T(r, t) = \frac{Q \exp\left(\frac{-r^2}{4at}\right)}{\rho c (4\pi at)^{\frac{1+n}{2}}}$	T relative to $T(t < 0)$. Planar case: $n=0$ and Q [J/m ²]. Cylindr. case: $n=1$ and Q [J/m]. Spherical case: $n=2$ and Q [J].

$$T(0,t) = \frac{Q}{\rho c (4\pi a t)^{\frac{1+n}{2}}}$$

$$\rho_i(r,t) = \frac{m_i \exp\left(\frac{-r^2}{4D_i t}\right)}{(4\pi D_i t)^{\frac{1+n}{2}}}$$

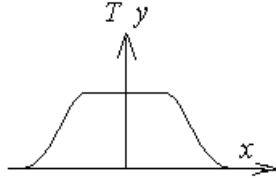
$$\rho_i(0,t) = \frac{m_i}{(4\pi D_i t)^{\frac{1+n}{2}}}$$

$t=0$, Delta(x).
 $t>0$, Gauss bell.

$$\int_V (T - T_0) dV = \frac{Q}{\rho c}$$

$$\int_V \rho_i dV = m_i$$

Instantaneous finite line-source, one-dimensional deposition of width L



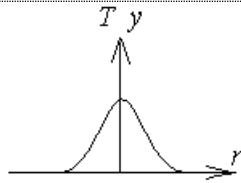
$$T(x,t) = \frac{Q}{2\rho c L} \left(\operatorname{erf}\left(\frac{\frac{L}{2} + x}{\sqrt{4\pi a t}}\right) + \operatorname{erf}\left(\frac{\frac{L}{2} - x}{\sqrt{4\pi a t}}\right) \right) \gg 0.$$

Tends to a point-source (Gauss bell) for $t \rightarrow \infty$

$$T(0,t) = \frac{Q}{L\rho c} \operatorname{erf}\left(\frac{L}{4\sqrt{a t}}\right)$$

$$y_i = \frac{y_{iL}}{2} \left(\operatorname{erf}\left(\frac{\frac{L}{2} + x}{\sqrt{4\pi D_i t}}\right) + \operatorname{erf}\left(\frac{\frac{L}{2} - x}{\sqrt{4\pi D_i t}}\right) \right)$$

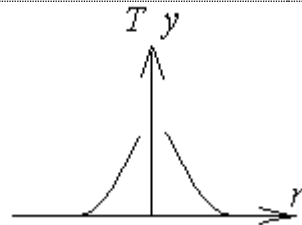
Continuous planar-source, one-dimensional deposition



$$T(x,t) = \frac{\dot{Q}\sqrt{t} \exp\left(\frac{-x^2}{4at}\right)}{2\rho c \sqrt{\pi a}}$$

$$T(0,t) = \frac{\dot{Q}\sqrt{t}}{2\rho c \sqrt{\pi a}}$$

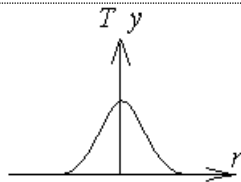
Continuous line-source deposition



$$T(r,t) = \frac{\dot{Q} \operatorname{Ei}\left(\frac{-r^2}{4at}\right)}{4\pi\rho c a}$$

Singular at $r=0$.
 For $r \ll \sqrt{4at}$,
 $\operatorname{Ei}(-x) \rightarrow -\gamma - \ln(x)$,
 with $\gamma=0.577$.

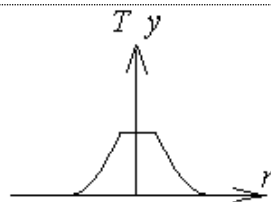
Continuous point-source, tri-dimensional deposition



$$T(r,t) = \frac{\dot{Q} \operatorname{erfc}\left(\frac{r}{\sqrt{4at}}\right)}{4\pi a \rho c r}$$

$$T(0,t) = \frac{\dot{Q}}{4\rho c (\pi a)^{3/2} \sqrt{t}}$$

Continuous spherical-source kept at fixed- T by controlling $\dot{Q}(t)$

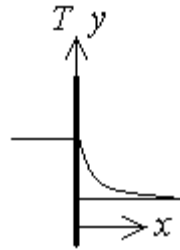


$$T(r,t) = T_R \frac{R}{r} \operatorname{erfc}\left(\frac{r-R}{\sqrt{4at}}\right)$$

$$\dot{Q}(t) = 4\pi R^2 T_R \left(\frac{1}{R} + \frac{1}{\sqrt{\pi a t}} \right)$$

Only valid for $r > R$.

Moving planar-source
one-dimensional
deposition



$$T = (T_0 - T_\infty) \exp\left(\frac{-xV}{a}\right)$$

$$y_i = (y_{i0} - y_{i\infty}) \exp\left(\frac{-xV}{D_i}\right)$$

$t < 0$:
 $T(x) = T_\infty, y_i(x) = y_{i\infty}$.
 $t > 0$:
 $T(0) = T_0, y_i(0) = y_{i0}$.

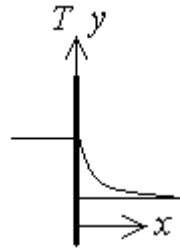
Moving point-source
tri-dimensional
deposition



$$T = \frac{\dot{q} \exp\left(\frac{-U_\infty(r-x)}{2a}\right)}{4\pi ar}$$

Only valid for steady
state ($t \rightarrow \infty$).
 $r^2 = x^2 + y^2 + z^2$.
 U_∞ is the constant
relative speed.

Planar contact with
forced jump at the
surface

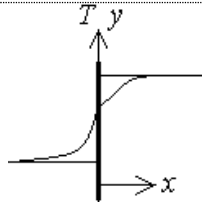


$$T = (T_0 - T_\infty) \operatorname{erfc}\left(\frac{x}{2\sqrt{at}}\right)$$

$$y_i = (y_{i0} - y_{i\infty}) \operatorname{erfc}\left(\frac{x}{2\sqrt{D_i t}}\right)$$

$t < 0$:
 $T(x) = T_\infty, y_i(x) = y_{i\infty}$.
 $t > 0$:
 $T(0) = T_0, y_i(0) = y_{i0}$.

Planar contact



$$T = A + B \operatorname{erf}\left(\frac{x}{2\sqrt{at}}\right)$$

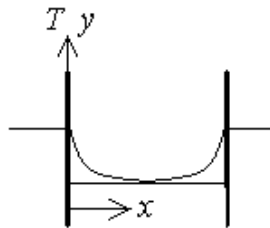
$$y_i = A + B \operatorname{erf}\left(\frac{x}{2\sqrt{D_i t}}\right)$$

$$T_0 = \frac{\sqrt{\rho_1 c_{p,1} k_1} T_1 + \sqrt{\rho_2 c_{p,2} k_2} T_2}{\sqrt{\rho_1 c_{p,1} k_1} + \sqrt{\rho_2 c_{p,2} k_2}}$$

$$y_{i0} = \frac{\rho_1 \sqrt{D_{i1}} y_{i1} + \rho_2 \sqrt{D_{i2}} y_{i2}}{\rho_1 \sqrt{D_{i1} k_1} + \rho_2 \sqrt{D_{i2} k_2}}$$

Contact value is T_0
for heat transfer, or
 y_{i0} for mass transfer.
 $t = 0$, Heaviside(x).
If equal properties:
 $T_0 = (T_1 + T_2)/2$ and
 $y_{i0} = (y_{i1} + y_{i2})/2$.

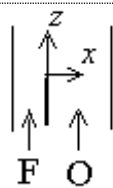
Continuous one-
dimensional planar
plate immersion



$$y_i = (y_{i0} - y_{i\infty}) \cdot \left\{ 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{\exp\left(-\frac{(2n+1)^2 \pi^2 D_i t}{L^2}\right)}{2n+1} \cdot \sin\left(\frac{(2n+1)\pi}{L} x\right) \right\}$$

$t < 0$:
 $T(x) = T_\infty, y_i(x) = y_{i\infty}$.
 $t > 0$:
 $T(0) = T_0, y_i(0) = y_{i0}$,
 $T(L) = T_0, y_i(L) = y_{i0}$.

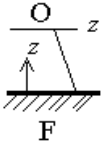
One-dimensional
planar contact, steady
in a moving frame
(e.g. mixing layer of
two equal-speed
streams)



$$y = A + B \operatorname{erf}\left(\frac{x}{2\sqrt{az/v}}\right)$$

It is the same as the
latter changing
 $t = z/v$, where v is the
common speed

One-dimensional planar steady diffusion through a wall or gap (e.g. evaporation from a test tube)



$$\frac{T - T_0}{T_1 - T_0} = \frac{z}{L}, \quad \dot{q} = -k \frac{T_1 - T_0}{L}$$

$$\frac{1 - y_i}{1 - y_{i0}} = \left(\frac{1 - y_{i1}}{1 - y_{i0}} \right)^{\frac{z}{L}} \xrightarrow{V \ll D_i/L}$$

$$\frac{y_i - y_{i0}}{y_{i1} - y_{i0}} = \frac{z}{L}, \quad j = -\rho D_i \frac{y_{i1} - y_{i0}}{L} = \rho V$$

interface equilibrium: $y_{i0} = \frac{M_v p_v^*(T)}{M_a p}$

Example: for 1 cm of air with given end values of T or y_i , there is $2,5 \text{ W} \cdot \text{m}^{-2} \cdot \text{K}^{-1}$ of heat flux, or 1 mm of liquid water evaporating per day

One-dimensional spherical steady diffusion (e.g. evaporation from a drop)



$$\frac{T - T_\infty}{T_0 - T_\infty} = \frac{r_0}{r}, \quad \dot{q} = -k \frac{T_0 - T_\infty}{r_0}$$

$$\frac{1 - y_i}{1 - y_{i\infty}} = \frac{1 - y_{i0}}{1 - y_{i\infty}} \left(\frac{r_0}{r} \right)^k \xrightarrow{V \ll D_i/L}$$

$$\frac{y_i - y_{i\infty}}{y_{i0} - y_{i\infty}} = \frac{r_0}{r}$$

$$j = -\rho D_i \frac{y_{i0} - y_{i\infty}}{r_0} = \rho V \Big|_{r=r_0} = \rho_{liq} \dot{r}_0$$

$$\dot{q} = -k \frac{T_0 - T_\infty}{r_0} = \rho_{liq} \dot{r}_0 h_{lv}$$

Example: a water droplet 1 mm in diameter with air at 50%RH lasts some 5000 s in evaporating, but a 0.1 mm droplet only 50 s, in both cases with some $\Delta T = 10 \text{ K}$ drop.

EVAPORATION RATE

An analysis of gas diffusion combined with evaporation from a condensate (valid for solids or liquids) can be found in [Combustion kinetics](#). We bring here just the result for a droplet evaporation lifetime:

$$t_{evap} = \frac{r_{0,ini}^2}{2 \frac{\rho}{\rho_{liq}} D_i \ln \frac{1 - y_{i\infty}}{1 - y_{i0}}} \quad (27)$$

with the equilibrium mass fraction of the vapours close to the liquid surface being:

$$y_{i0} = x_{i0} \frac{M_i}{M_m} = \frac{p_i^*(T_{liq})}{p} \frac{M_i}{M_m} \quad (28)$$

x_{i0} being the vapour molar fraction, which for ideal mixtures is given by Raoult's law in terms of the pure-component vapour pressure (M_i and M_m are the molar mass of the diffusing species and of the mixture, respectively). Far in the atmosphere, the concentration of the diffusing species is usually zero, or some environmental data, like relative humidity for water vapour:

$$y_{i\infty} = x_{i\infty} \frac{M_i}{M_m} = \frac{\phi_\infty p_i^*(T_{amb})}{p} \frac{M_i}{M_m} \quad (29)$$

Equation (27) can be explained (and memorised) with the help of an order-of-magnitude analysis, in the following way. The time for diffusion of a gas puff of characteristic size $r_{0,ini}$ with a high concentration of species i , y_{iw} , within a gas mixture with lower concentration of i , $y_{i\infty}$, would arrange to yield a mass-Fourier number of order unity, i.e. $t_{dif}=r_{0,ini}^2/(D_i\Delta y_i)$, and taking into account the fact that the puff is condensed, the lifetime (for evaporation, now) will be proportional to the density ratio, thus $t_{evap}=r_{0,ini}^2/((\rho/\rho_{liq})D_i\Delta y_i)$, a rather accurate approximation to the exact result (27); just a numeric factor, since for $y_i \ll 1$, $\ln((1-y_{i\infty})/(1-y_{i0})) \rightarrow y_{i\infty}-y_{i0}$.

Another way to produce (27) is by heat-transfer analogy. In effect, for heat diffusion from a hot sphere we know that the Nusselt number is $Nu=2$ (what can also be checked from any heat convection correlation around a sphere at very low Reynolds numbers). Thence, the Sherwood number (see Non-dimensional parameters in Heat and Mass Convection) is $Sh=h_m L/(\rho D_i)=2$, with the characteristic length being $L=D=2r_0$ in this case; i.e.:

$$\begin{aligned} \dot{m}_i &= h_m A (y_{iw} - y_{i\infty}) = -A \rho D_i \left. \frac{\partial y_i}{\partial r} \right|_{r_0} = \rho_{liq} A \frac{dr_0}{dt} \xrightarrow{Sh = \frac{h_m D}{\rho D_i} = 2} \\ \Rightarrow \frac{2 \rho D_i}{2 r_0} (y_{iw} - y_{i\infty}) &= \rho_{liq} \frac{dr_0}{dt} \Rightarrow t_{evap} = \frac{r_0^2}{2 \frac{\rho}{\rho_{liq}} D_i (y_{iw} - y_{i\infty})} \end{aligned} \quad (30)$$

For instance, for the lifetime for a 0.1 mm in diameter water droplet in ambient air at 25 °C and 50%HR, we get $t_{evap}=4.3$ s, with $r_0=50 \cdot 10^{-6}$ m, $\rho=\rho_{air}=1.2$ kg/m³, $\rho_{liq}=1000$ kg/m³, $D_i=24 \cdot 10^{-6}$ m²/s (Table 2 above), $y_{i\infty}=0.01$ and $y_{i0}=(p^*/p)(M_i/M_m)=(3.17/100)(0.018/0.029)=0.02$

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