Materials Engineering (MED 123)

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The Boltzmann-Matano method

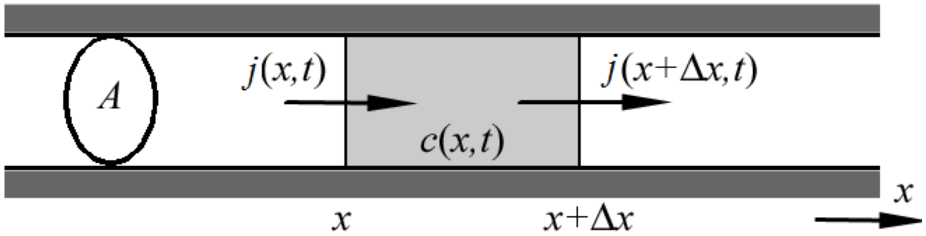
- The method is used to calculate the diffusion coefficient D (or thermal diffusivity a) as a function of concentration C (temperature T) in a 1D transport of mass
- It converts the diffusion equation

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left[D(C)\,\frac{\partial C}{\partial x}\right]$$

  into a more easily solved ordinary differential equation
- The rudiments of the method were proposed by L. Boltzmann
  - Austrian physicist (1844 –1906) known especially for developing the theory of statistical mechanics
- C. Matano determined experimentally the diffusion coefficients as a function of concentration in metal alloys
  - Japanese physicist (1905 – 1947) who also studied fibers

- The diffusion equation expresses the **conservation of mass**
- In any short portion (between x and $x + \Delta x$) of a 1D domain the mass balance may be expressed as

$$(\text{time change in mass}) = (\text{flow inside}) - (\text{flow outside})$$



- Thus,

$$V \frac{\Delta C}{\Delta t} = j(x)\,A - j(x + \Delta x)\,A$$

- Since $V = A\Delta x$, we further get

$$\frac{\Delta C}{\Delta t} = \frac{j(x) - j(x + \Delta x)}{\Delta x}$$

- For very small Δx and Δt, this becomes

$$\frac{\partial C}{\partial t} = -\frac{\partial j}{\partial x} = \frac{\partial}{\partial x}\left(D\,\frac{\partial C}{\partial x}\right)$$

- Finally, using Fick's first law $j = -D(\partial C/\partial x)$, we get the diffusion equation

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D\,\frac{\partial C}{\partial x}\right)$$

Parabolic law

- What is the time t needed for a given concentration value to arrive at a certain position x?

- This time is proportional to the square of the distance,

$$t \propto x^2$$

(this is usually called the parabolic law — recall that a parabola is a graph of a quadratic function)

- In other words, advancement of a concentration front is proportional to the square root of time

$$x \propto \sqrt{t}$$

- Therefore, in diffusion processes the concentration $C(x, t)$ should depend on x and t via a quantity $x/\sqrt{t}$

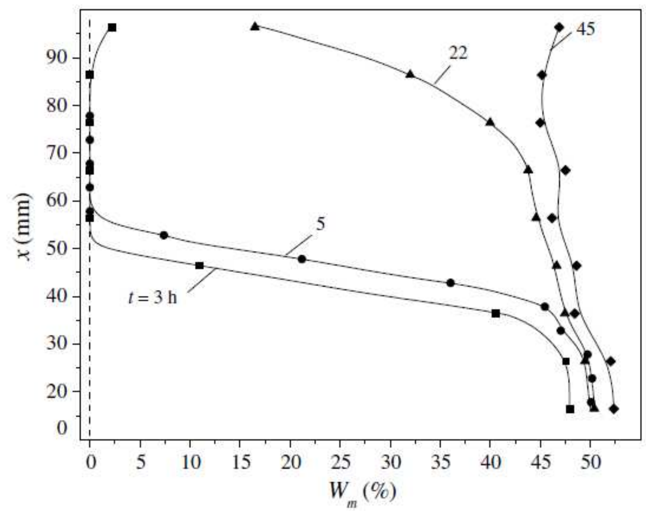
- **Conclusion:** Use the transformation

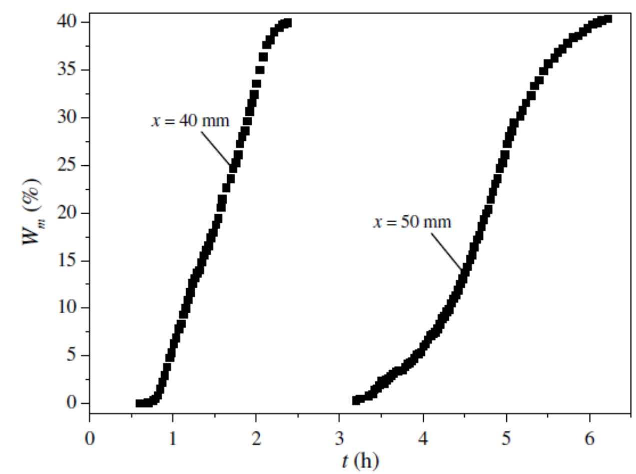
$$\boxed{\eta = \frac{x}{\sqrt{t}}}$$

in diffusion equation — it should be then easier to describe

Example experiment

- Example of profiles for the moisture content W_m (plays the role of the concentration C) in a porous concrete
- Taken from M.I. Nizovtsev et al., *International Journal of Heat and Mass Transfer* 51 (2008) 4161–4167





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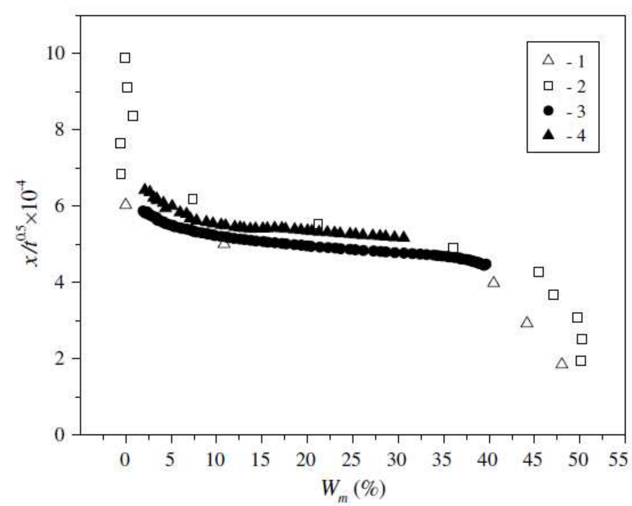


- Apply the Boltzmann transformation

$$\eta = \frac{x}{2\sqrt{t}}$$

- Then the diffusion equation becomes

$$\boxed{-2\eta \frac{dC}{d\eta} = \frac{d}{d\eta}\left[D(C)\,\frac{dC}{d\eta}\right]}$$

- This is an **ordinary** differential equation, unlike the diffusion equation (which is a partial differential equation): this time $C = C(\eta)$ is only a function of η

- **Note:** A trivial solution is $C(\eta) = \mathrm{const}$ (i.e., concentration is constant over η).
- This can be interpreted as the time necessary for a concentration front to arrive at a certain position being proportional to the square of the distance, $t \propto x^2$
- In this way we may justify the parabolic law

- The diffusion equation reads

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left[D(C)\,\frac{\partial C}{\partial x}\right],$$

where $C = C(x, t)$ is a function of space and time

- Apply the Boltzmann transformation

$$\eta = \frac{x}{2\sqrt{t}}$$

- Then the time and space derivatives can be written as η derivatives:

$$\frac{\partial}{\partial t} = \frac{\partial \eta}{\partial t}\,\frac{d}{d\eta} = -\frac{x}{4(\sqrt{t})^3}\,\frac{d}{d\eta} = -\frac{\eta}{2t}\,\frac{d}{d\eta}$$

$$\frac{\partial}{\partial x} = \frac{\partial \eta}{\partial x}\,\frac{d}{d\eta} = -\frac{1}{2\sqrt{t}}\,\frac{d}{d\eta},$$

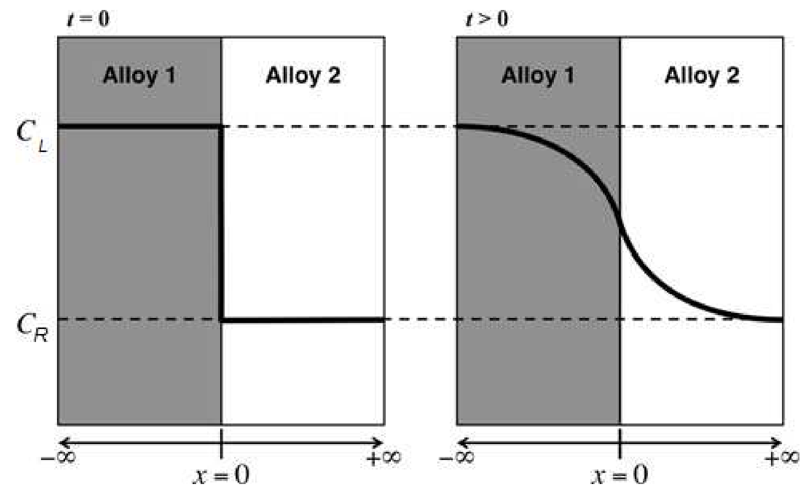
- And the diffusion equation becomes

$$-\frac{\eta}{2t}\,\frac{dC}{d\eta} = -\frac{1}{2\sqrt{t}}\,\frac{d}{d\eta}\left[D(C)\left(-\frac{1}{2\sqrt{t}}\,\frac{dC}{d\eta}\right)\right];$$

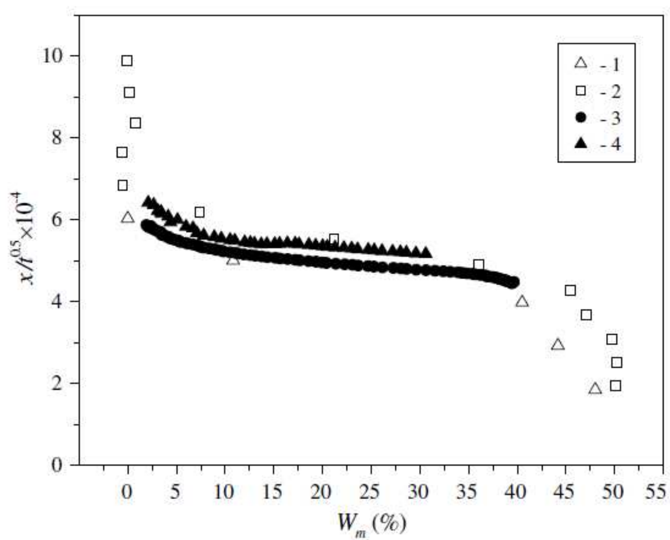
i.e.,

$$-2\eta\,\frac{dC}{d\eta} = \frac{d}{d\eta}\left[D(C)\,\frac{dC}{d\eta}\right]$$

- Profiles $C(\eta)$ are often S-shaped:



- Or, recall the experiment from p. 6:



- For S-shaped profiles a *convenient approximation* is

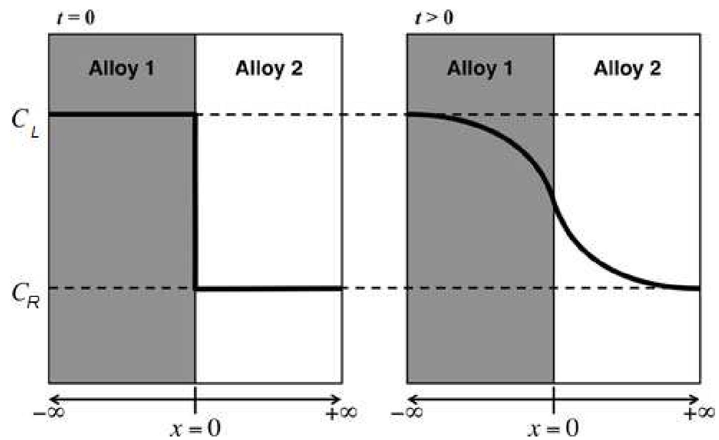
$$C(x,t) = \frac{C_L + C_R}{2} + \frac{C_R - C_L}{2}\,\operatorname{erf} y$$

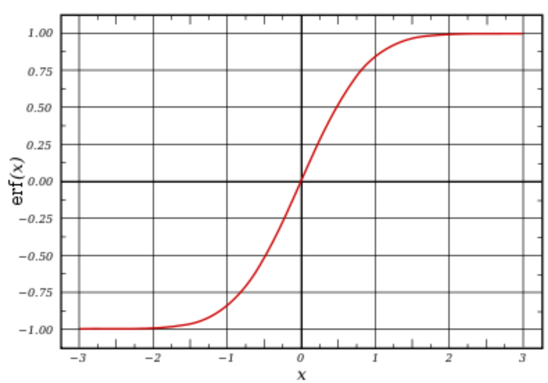
- Here a is a parameter and erf is the error function that may be defined as the sum

$$\operatorname{erf} y = \frac{2}{\sqrt{\pi}}\left(y - \frac{y^3}{5} + \frac{y^5}{10} - \frac{y^7}{42} + \frac{y^9}{216} - \cdots\right) = \frac{2}{\sqrt{\pi}}\sum_{n=0}^{\infty}(-1)^n\frac{y^{2n+1}}{n!(2n+1)}$$

- You may compare it with, say, the sum for sine:

$$\sin y = y - \frac{y^3}{3!} + \frac{y^5}{5!} - \frac{y^7}{7!} + \frac{y^9}{9!} - \cdots = \sum_{n=0}^{\infty}(-1)^n\frac{y^{2n+1}}{(2n+1)!}$$





- It turns out that the erf approximation

$$C = \frac{C_L + C_R}{2} + \frac{C_R - C_L}{2} \operatorname{erf} y \qquad \text{with} \qquad y = \frac{\eta}{\sqrt{D}} = \frac{x}{2\sqrt{Dt}}$$

  is a **solution** to the diffusion equation

$$-2\eta \frac{dC}{d\eta} = \frac{d}{d\eta}\left[D \frac{dC}{d\eta}\right], \qquad \text{or} \qquad -2\eta \frac{dC}{d\eta} = D \frac{d^2C}{d\eta^2}$$

  in which the diffusion coefficient D is a **constant**

- Note that concentration C depends on x and t again via a quantity $x/\sqrt{t}$
- There are also other known solutions to the diffusion equation, depending on the initial and boundary conditions

- We plug
$$C(\eta) = \frac{C_L + C_R}{2} + \frac{C_R - C_L}{2} \, \mathrm{erf}\, y \qquad \text{with} \qquad y = \frac{\eta}{\sqrt{D}}$$
into the diffusion equation
$$-2\eta \, \frac{dC}{d\eta} = D \, \frac{d^2 C}{d\eta^2}$$
and see whether the LHS is equal to the RHS

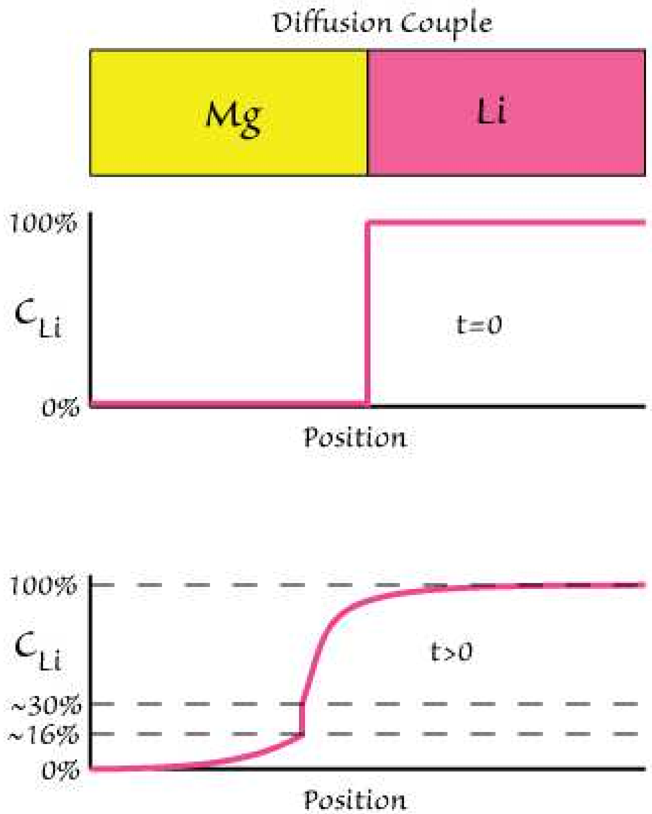
- We use that the derivative of erf is the Gaussian bell
$$\frac{d \, \mathrm{erf}\, y}{dy} = \frac{2}{\sqrt{\pi}} \, e^{-y^2}$$

- Thus,
$$\frac{dC}{d\eta} = \frac{C_R - C_L}{2} \, \frac{2}{\sqrt{\pi D}} \, e^{-\eta^2/D}, \qquad \frac{d^2 C}{d\eta^2} = \frac{C_R - C_L}{2} \, \frac{2}{\sqrt{\pi D}} \left(- \frac{2\eta}{D} \right) e^{-\eta^2/D}$$

- Consequently,
$$\mathrm{LHS} = -2\eta \frac{C_R - C_L}{2} \, \frac{2}{\sqrt{\pi D}} \, e^{-\eta^2/D}$$
and
$$\mathrm{RHS} = D \, \frac{C_R - C_L}{2} \, \frac{2}{\sqrt{\pi D}} \left(- \frac{2\eta}{D} \right) e^{-\eta^2/D},$$

- We see that LHS = RHS

- In 1933 Matano applied the transformed equation to study diffusion in alloys
- In his experiment two alloys with different concentration of diffusing atoms are put into contact and the concentration C at a fixed time t can be extracted as a function of the x coordinate.
- Example of a diffusion couple — magnesium + lithium:



- To obtain a formula for the diffusion coefficient D, let us integrate the equation

$$-2\eta \frac{dC}{d\eta} = \frac{d}{d\eta}\left[D(\eta)\frac{dC}{d\eta}\right]$$

over η from a chosen value $\eta = \eta^*$ to $\eta = \infty$ (where $C = C_R$)

- We get

$$-2\int_{\eta^*}^{\infty} \eta \frac{dC}{d\eta}\, d\eta = \left[D(\eta)\frac{d(C-C_R)}{d\eta}\right]_{\eta^*}^{\infty} = -D(\eta^*)\left\{\frac{d(C-C_R)}{d\eta}\right\}_{\eta=\eta^*}$$

- Therefore,

$$\boxed{D(\eta^*) = \frac{2\int_{\eta^*}^{\infty} \eta \frac{dC}{d\eta}\, d\eta}{\left\{\frac{d(C-C_R)}{d\eta}\right\}_{\eta=\eta^*}}}$$

- If we **know the concentration profile** $C(\eta)$ from experiment, then we can **calculate** the integral in the nominator and the derivative in the denominator, and the formula yields the value of **the diffusion coefficient** D at $\eta = \eta^*$ $\longrightarrow$ we get the dependence of D on η

- Subsequently, if we express η via C (by inverting the profile $C(\eta)$), then from $D(\eta)$ we get the desired dependence of D on the concentration C

- These calculations are usually performed numerically

- For the considered profile for the moisture content W_m (that plays the role of the concentration C), the resulting dependence of the moisture diffusion coefficient D_m on the moisture content W_m is: