Transport phenomena

T1. The laws of diffusion

If gradients of concentration exist for a component, there will be a migration of the particles towards a region of lower concentration. This is called ***diffusion.***

Diffusion occurs along the gradient of the chemical potential (partial molar Gibbs free energy). The definition of chemical potential of component i:

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T,p,n_j,j \neq i} \qquad \text{(T1)}$$

Diffusion is described by Fick's laws.

Fick's first law (in one dimension). If there is an inhomogenity of concentration in direction x, there will be a migration of molecules towards the lower concentrations. The velocity of the migration of the amount of substance through a suface A (which is perpendicular to the direction of migration) is proportional to

i) the derivative of the concentration with respect to x and

ii) the surface area.

$$\frac{dn}{dt} = -D \cdot A \cdot \frac{dc}{dx} \qquad [\mathrm{mol \cdot s^{-1}}] \qquad (T2)$$

where D [$m^2 \cdot s^{-1}$] is the diffusion coefficient.

The flux (j_n) is defined as the velocity of migration of amount of substance through a surface of unit area:

$$j_n = \frac{1}{A} \cdot \frac{dn}{dt} \left[mol \cdot m^{-2} \cdot s^{-1} \right] \qquad \text{(T3)}$$

So Fick's first law in terms of flux:

$$j_n = -D \cdot \frac{dc}{dx} \qquad \text{(T4)}$$

The negative sign in Fick's first law indicates that the direction of the flux is opposite to the concentration gradient.

Fick's first law (in three dimensions). If there is an inhomogenity of concentration in all the three (x, y and, z) dimensions, the direction of the flux is opposite to the gradient of concentration.

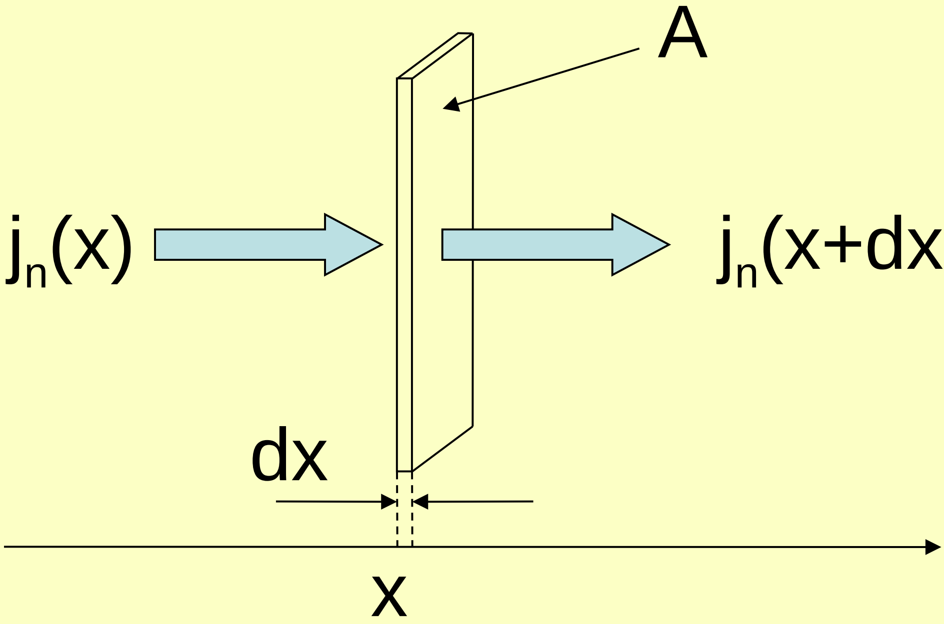
$$j_n = -D \cdot grad\ c \qquad \text{(T5)}$$

where

$$grad\ c = \frac{\partial c}{dx} \cdot i + \frac{\partial c}{dy} \cdot j + \frac{\partial c}{dz} \cdot k$$

Here, ***i, j,*** *and* ***k*** *are unit vectors in the directions of x, y, and z, respectively*.

Derivation of Fick's second law. Consider a thin slice of the solution of cross sectional area A between x and x+dx. Its volume is $dV = A \cdot dx$.



The change of the amount of substance in unit time in the elementary volume is $A \cdot [j_n(x) - j_n(x+dx)]$.

$$\frac{\partial n}{\partial t}=A\left[j_n[x]-j_n(x+dx)\right]$$

The change of concentration:

$$\frac{\partial c}{\partial t}=\frac{1}{dV}\cdot A\cdot\left[j_n(x)-j_n(x+dx)\right]$$

$j_n(x+dx)$ can be expressed as

$$j_n(x+dx)=j_n(x)+\frac{\partial j_n}{\partial x}\cdot dx$$

Substituting it into the previous equation:

$$\frac{\partial c}{\partial t}=\frac{1}{\cancel{A\cdot dx}}\cdot\cancel{A\cdot}\left[j_n\cancel{(x)}-j_n\cancel{(x)}-\frac{\partial j_n}{\partial x}\cdot\cancel{dx}\right]$$

$$\frac{\partial c}{\partial t} = -\frac{\partial j_n}{\partial x}$$

Fick’s first law:

$$j_n = -D \cdot \frac{dc}{dx}$$

$$\frac{\partial c}{\partial t} = D \cdot \frac{\partial^2 c}{\partial x^2} \qquad (T6)$$

This is Fick’s second law in one dimension.

In three dimensions:

$$\frac{\partial c}{\partial t} = D \cdot \left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2} \right) \qquad (T7)$$

Fick's second law shows the relationship between the time- and spatial dependence of the concentration:

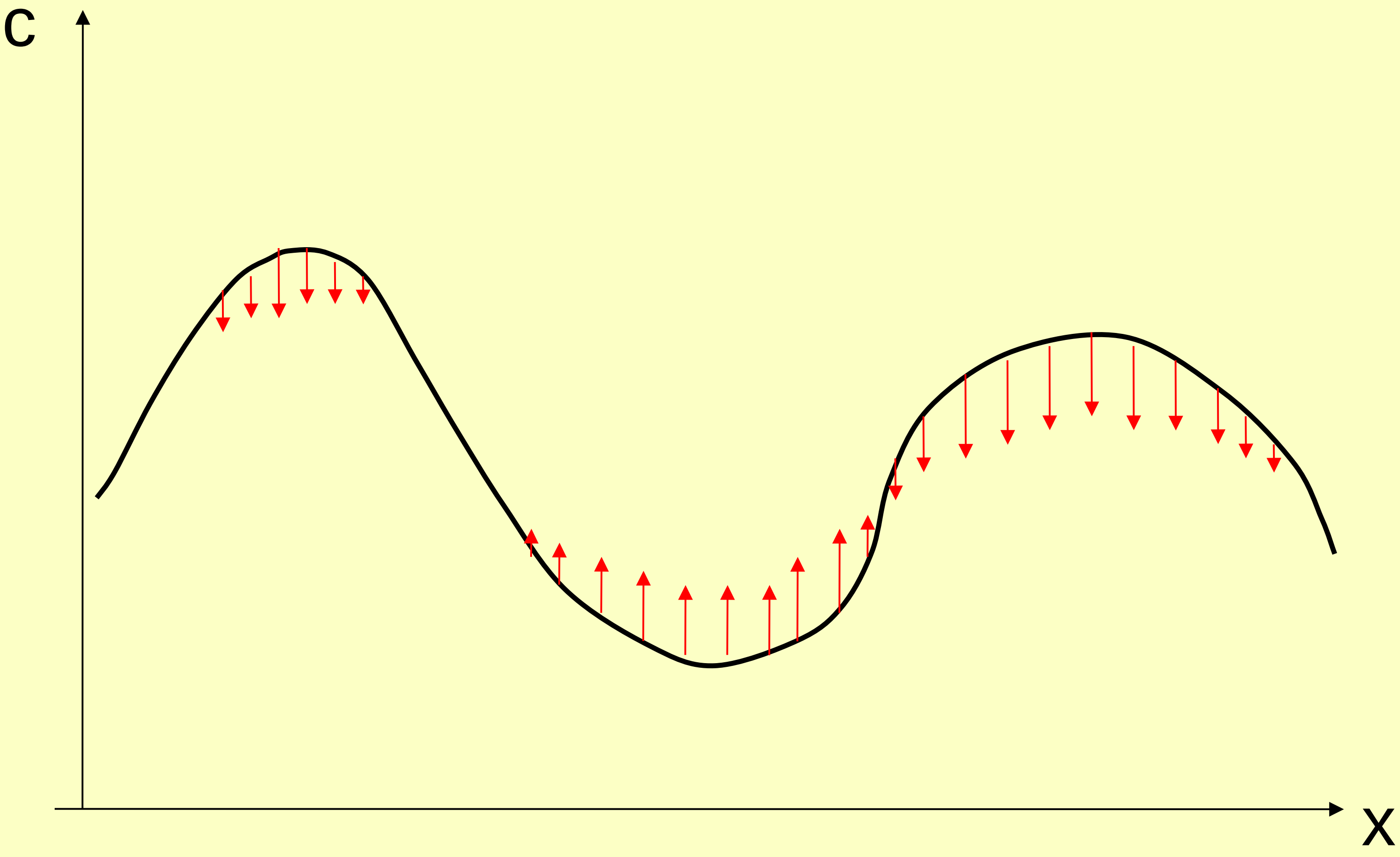
$$\frac{\partial c}{\partial t} = D \cdot \frac{\partial^2 c}{\partial x^2}$$

According to this equation (T6), if the second derivative with respect to x is positive, the concentration increases in time.

If the second derivative with respect to x is negative, the concentration decreases in time.

The following figure shows how the concentration changes in time and space.

The arrows show how the concentration changes in time.



In regions where the concentration changes linearly with x, there is an inflection, and the concentration does not change in time.

The slope of the tangent gives first derivative,

$$\frac{\partial c}{\partial x}$$ Its value decreases until the inflection point.

From this point, its value increases, at first, it has a negative sign but from the minimum point up, its sign is positive.

The decrease of the first derivative refers to the negative sign of the second derivative, while its increase means positive sign of $$\frac{\partial^2 c}{\partial x^2}$$

i.e., the red arrows on the figure point downwards and upwards, respectively. See equation T6.

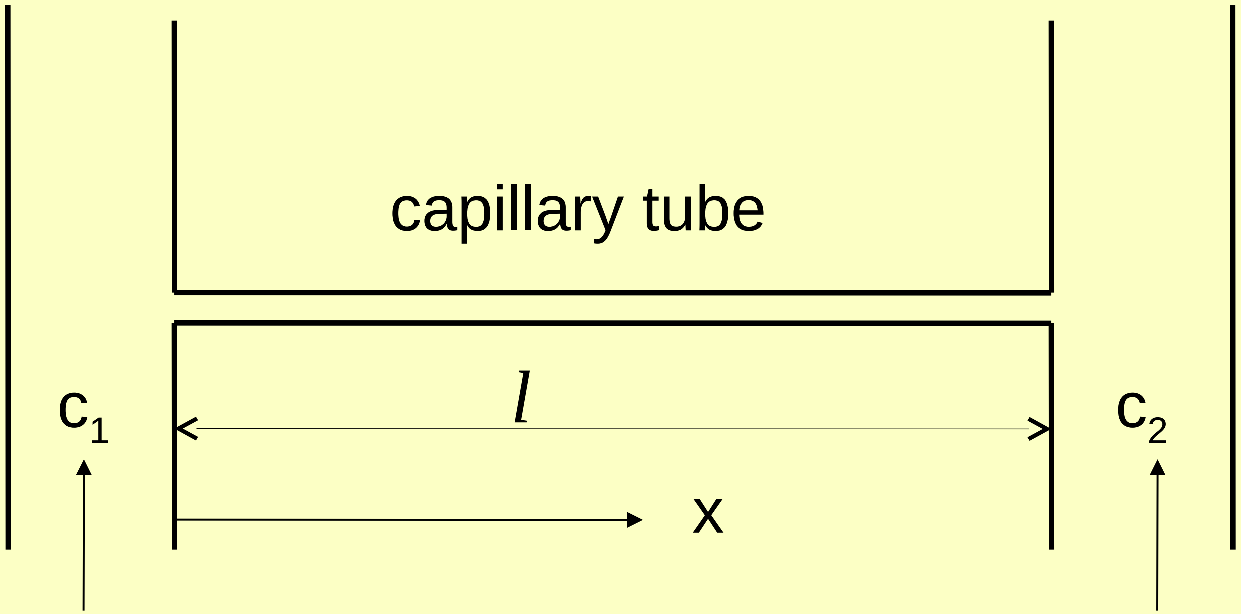
T2. Steady state diffusion

In a steady state process, the parameters (pressure, temperature, concentrations, etc.) are independent of time – they are functions of space only.

Modern industrial production lines work continuously, and they approach steady state conditions.

In the following experiment, the diffusion along the capillary tube is steady state.

The continuous flow of liquids (or gases) in the thick tubes ensures the constant concentrations c_1 and c_2 at the two ends of the capillaty tube, respectively.



If $c_2 > c_1$, there is a diffusion from right to left along the capillary.

If steady state is attained, $$\frac{\partial c}{\partial t}=0$$

Therefore, according to Fick's second law (T6)

$$\frac{\partial c}{\partial t}=D\cdot\frac{\partial^2 c}{\partial x^2}=0$$

Since D $\neq$ *0,* $\frac{\partial^2 c}{\partial x^2}=0$ *The solution of this differential equation is a linear function.*

Integrate once, $\frac{\partial c}{\partial x}=a$ *(constant)*

Integrate second time, $c=a\cdot x+b$

To determine constants a and b consider the boundary conditions:

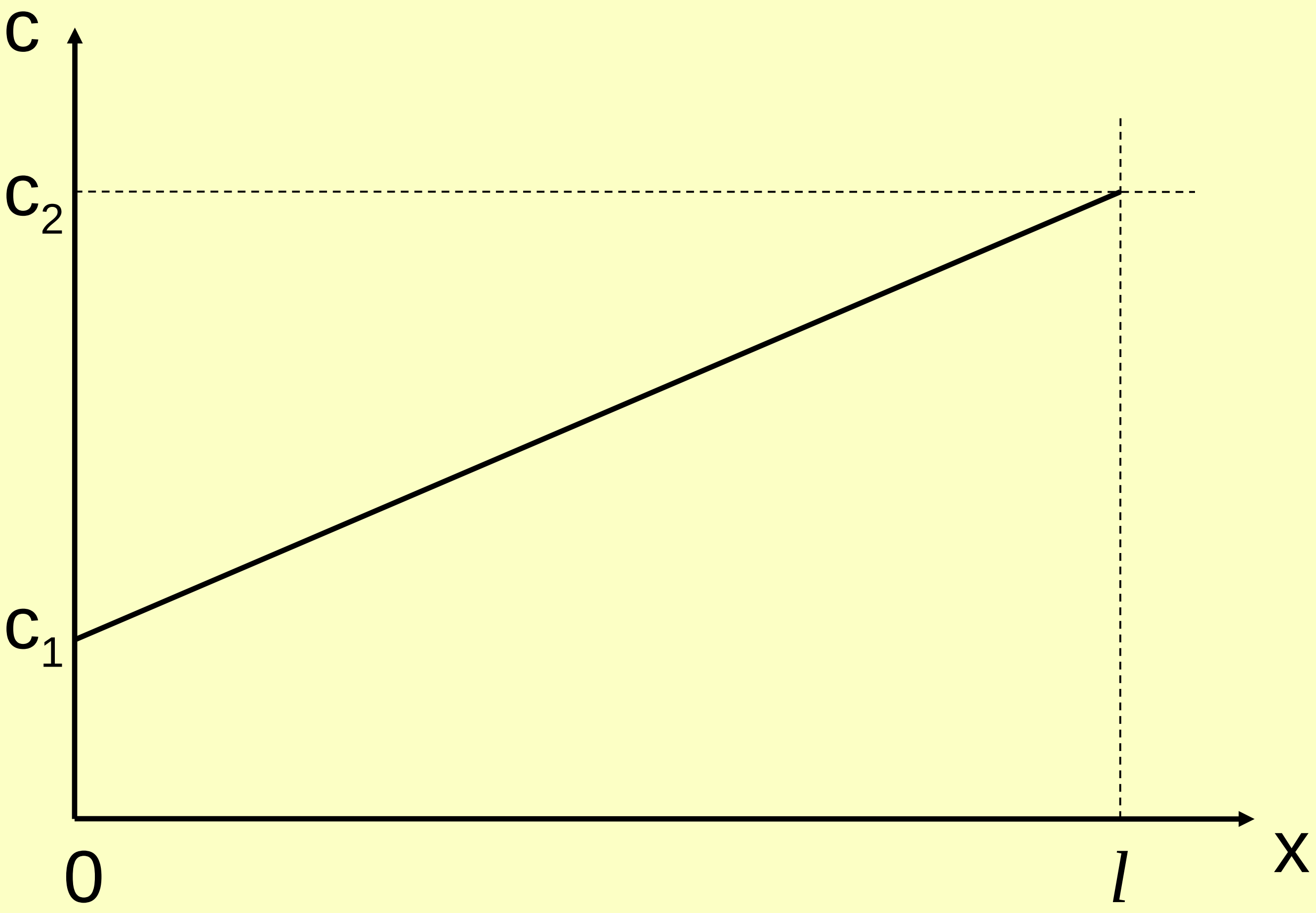
If $x = 0$, $c = c_1$ $c_1 = a \cdot 0 + b$ $b = c_1$

If $x = l$, $c = c_2$ $c_2 = a \cdot l + c_1$ $a = (c_2 - c_1)/l$

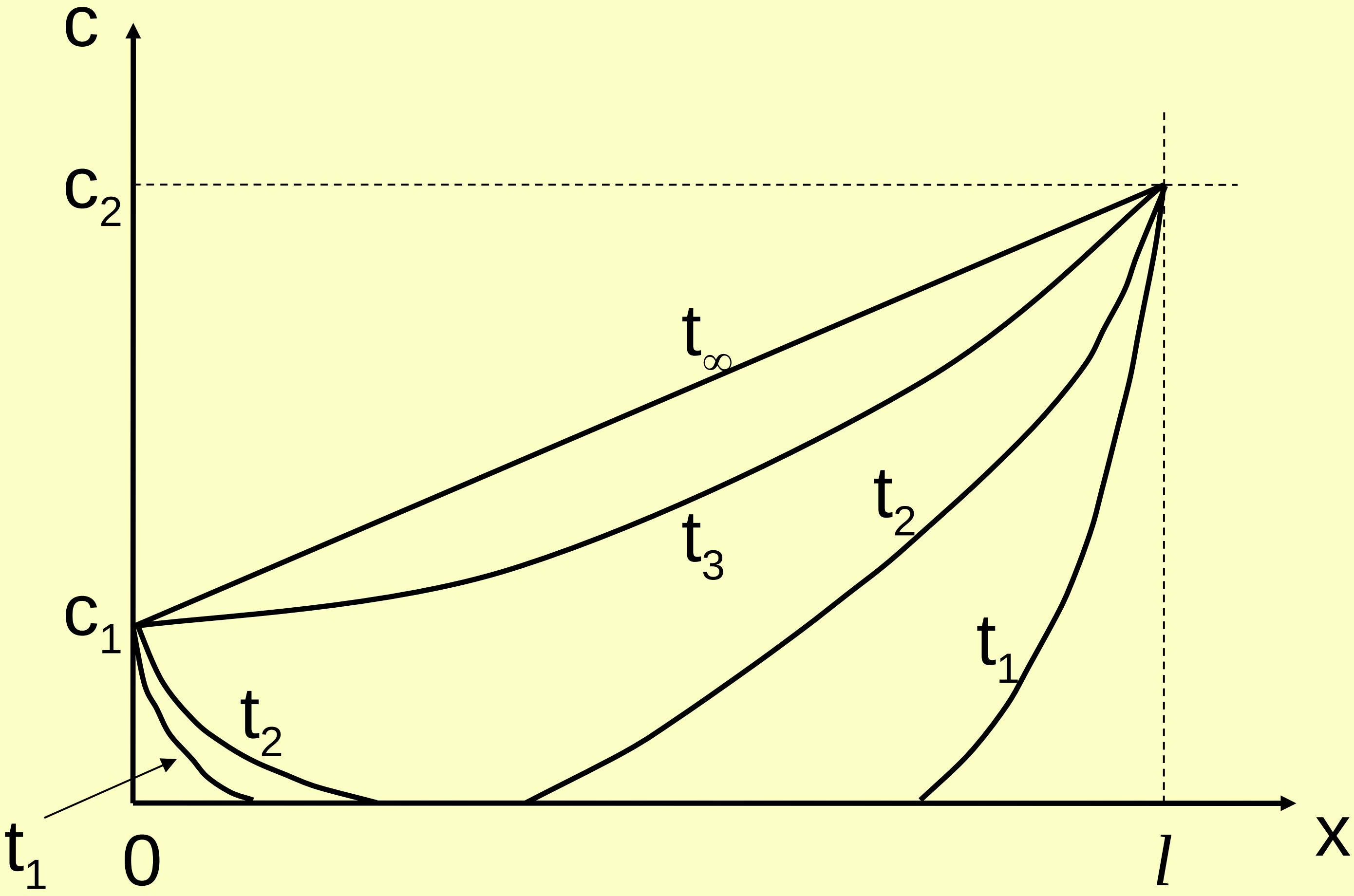
So the equation describing the dependence of concentration on x:

$$c = c_1 + \frac{c_2 - c_1}{l} \cdot x \qquad (T8)$$

The steady state concentration in the capillary (as function of x)



The following diagram shows how steady state is reached if there is pure solvent in the capillary initially.



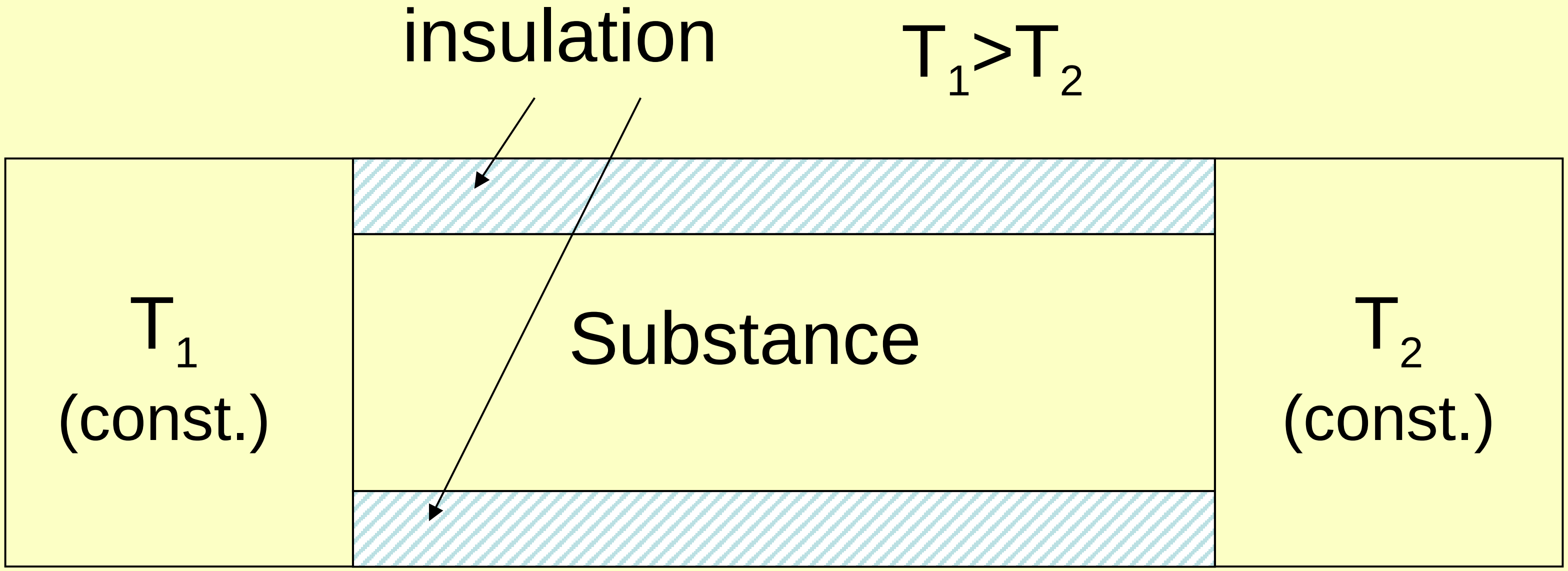
$0<t_1<t_2<t_3<t_\infty$

T3. Heat conduction

Heat conduction is the transport of internal energy.

If there is a temperature gradient in a substance, there is a heat flow from the point of higher temperature to the point of lower temperature.

Let us connect two bodies of different temperature through a third body, a bar. The material of the bar is the studied substance.



Fourier's law of heat (q) conduction (one dimension):

$$\frac{dq}{dt} = -\lambda \cdot A \cdot \frac{dT}{dx}$$

where dq/dt is the heat flow in unit time through a cross section A, dT/dx is the temperature gradient.

(T9)

λ [J/(m · s · K)] *is the thermal conductivity*

Fourier's law is very similar to Fick's first law.

The heat flow in unit time and unit cross section is called the heat flux j_q.

$$j_q = \frac{1}{A} \cdot \frac{dq}{dt} \left[Joule \cdot m^{-2} \cdot s^{-1} \right]$$

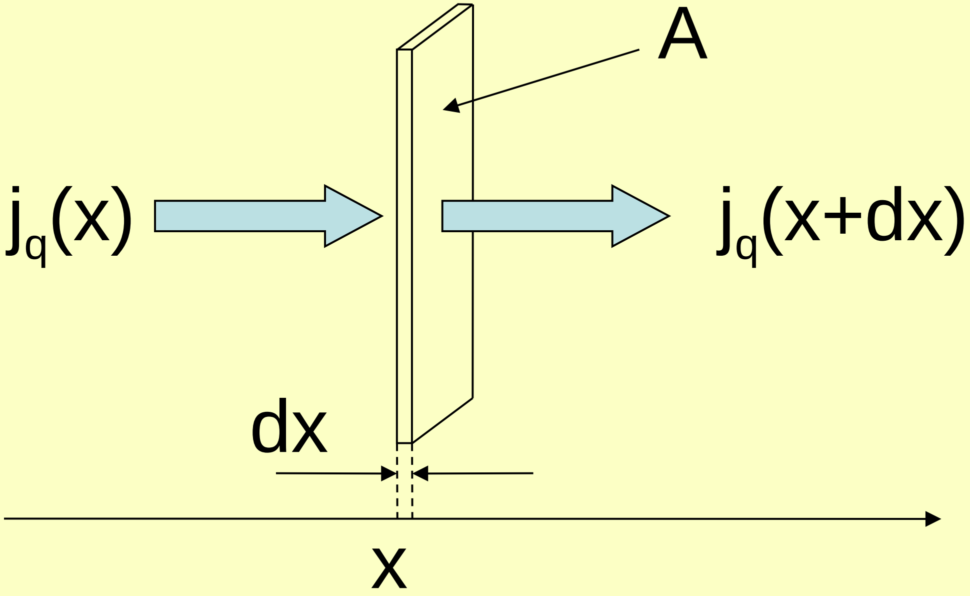
Fourier's law for heat flux:

$$j_q = -\lambda \cdot \frac{dT}{dx} \qquad \textit{(T10a)}$$

In three dimensions:

$$j_q = -\lambda \cdot grad\ T \qquad \text{(T10b)}$$

An expression similar to Fick's second law can also be derived. Consider a thin slice of the heat conductor of cross sectional area A between x and x+dx. Its volume is $dV = A \cdot dx$.



The change of the internal energy in unit time in the elementary volume is

$$\frac{dQ}{dt}=A\cdot\left[j_q(x)-j_q(x+dx)\right]$$

where Q=q(x)-q(x+dx)

Note that dQ/dt is also an infinitesimal quantity.

$j_q(x+dx)$ *can be expressed as*

$$j_q(x+dx)=j_q(x)+\frac{\partial j_q}{\partial x}\cdot dx$$

Substituting it into the previous equation:

$$\frac{dQ}{dt}=A\cdot\left[\cancel{j_q(x)}-\cancel{j_q(x)}-\frac{\partial j_q}{\partial x}\cdot dx\right]$$

$$\frac{dQ}{dt} = -A \cdot \frac{\partial j_q}{\partial x} \cdot dx$$

Fourier's law: $j_q = -\lambda \cdot \frac{dT}{dx}$

$$\frac{dQ}{dt} = \lambda \cdot A \cdot \frac{\partial^2 T}{\partial x^2} \cdot dx$$

Consider that $A \cdot dx = dV$ *and* $dQ = c \cdot dm \cdot dT$*; where* *m is the mass, c [J ·kg^{-1} ·K^{-1}] is the specific heat:*

$$c \cdot dm \cdot \frac{dT}{dt} = \lambda \cdot \frac{\partial^2 T}{\partial x^2} \cdot dV$$

If we substitute dm/dV = ρ *(density), we obtain the final form:*

$$\frac{dT}{dt} = \frac{\lambda}{\rho \cdot c} \cdot \frac{\partial^2 T}{\partial x^2} \qquad \text{(T11a)}$$

In three dimensions:

$$\frac{dT}{dt} = \frac{\lambda}{\rho \cdot c} \cdot \left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} \right) \qquad \text{(T11b)}$$

This equation connects the time dependence and spatial dependence of the temperature. It is similar to Fick’s second law (T6). The concentration is replaced by the temperature and the diffusion coefficient D is replaced by $\lambda/(\rho\cdot c)$ where λ is the thermal conductivity, ρ is the density and c is the specific heat.

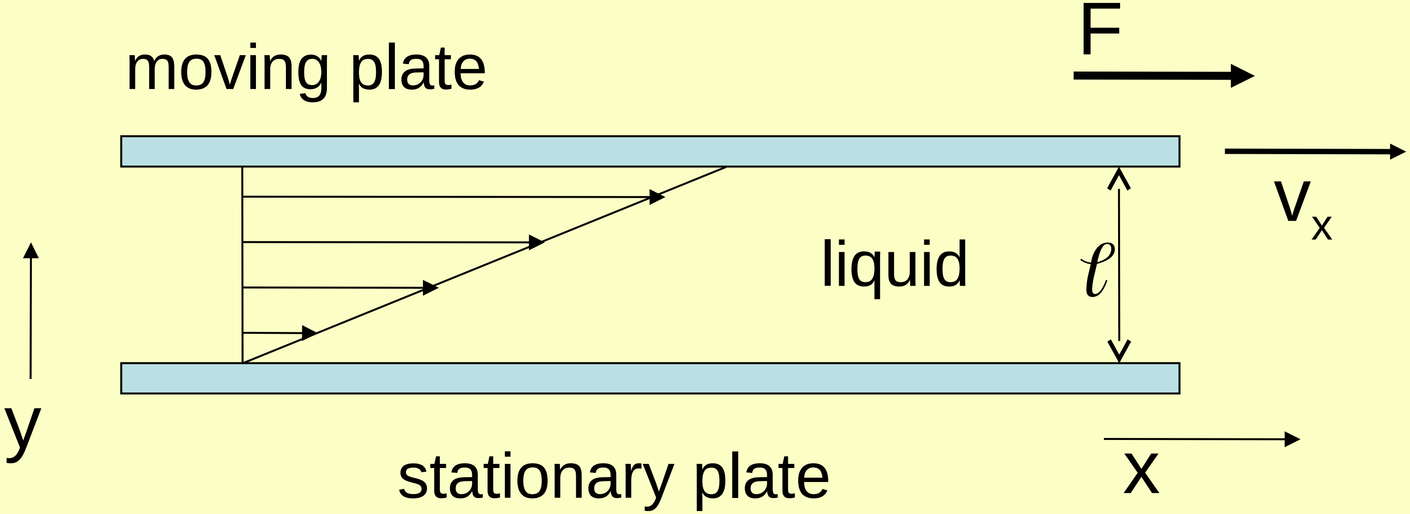
$$\frac{\partial c}{\partial t} = D\cdot\frac{\partial^2 c}{\partial x^2}$$

and

$$\frac{dT}{dt} = \frac{\lambda}{\rho\cdot c}\cdot\frac{\partial^2 T}{\partial x^2}$$

4. Viscosity

Consider two plates at distance ℓ from each other. The space in between is filled with a liquid (or a gas). One plate is stacionary, the other is moving in direction x at a velocity of v_x, and a force F acts.



The liquid layer in the proximity of the moving plate is attached to it and moves with velocity v_x. Similarly, a layer is also attached to the stationary plate.

Between the two plates, the velocity of the liquid layers increases gradually from zero to v_x as y increases from zero to ℓ. We assume laminar flow, i. e., there is no material flow between the neighboring layers.

The force F that has to be overcome to move the plate is proportional to the area (A), the velocity (v_x), and inversely proportional to the distance.

$$F_x = -\eta \cdot A \cdot \frac{v_x}{\ell} = -\eta \cdot A \cdot \frac{dv_x}{dy} \qquad \text{(T12)}$$

This is Newton’s law of viscosity.

The proportionality factor η is called the ***viscosity*** of the liquid. The dimension of η is (force $\cdot$ time)/area.

The minus sign expresses that the direction of the force arising is opposite to the direction of the velocity.

The SI unit of η is $\mathrm{Pa \cdot s = kg \cdot m^{-1} \cdot s^{-1}}$.

The old (CGS) unit is called Poise.

1 Poise = $\mathrm{1\ g \cdot cm^{-1} \cdot s^{-1} = 0.1\ Pa \cdot s}$.

Viscous flow is a transport phenomenon (as diffusion and heat conduction)

It is a transport of ***momentum*** (p = m·v) from the faster to the slower moving layers as can be seen from the following consideration.

$$F_x = m \cdot a_x = m \cdot \frac{dv_x}{dt} = \frac{d\left(m \cdot v_x\right)}{dt} = \frac{dp_x}{dt} = -\eta \cdot A \cdot \frac{dv_x}{dy}$$

dp_x/dt is the transport of momentum in unit time in the direction of y.

If we divide F_x by the area (A), we obtain the ***flux of momentum*** (j_p).

$$j_p = -\eta \cdot \frac{dv_x}{dy} \qquad \text{(T13)}$$

The unit of flux of momentum is

$(kg \cdot m \cdot s^{-1}) \cdot m^{-2} \cdot s^{-1} = kg \cdot m^{-1} \cdot s^{-2}$.

Those liquids that obey Newton’s law are called ***Newtonian liquids***.

Those liquids that do not obey Newton’s law are called ***non-Newtonian liquids: viscosity depends on time*** (*suspensions, like toothpaste or blood).*

The mechanism of viscous flow of liquids and gases is different.

Common features:

a) In both cases each layer performs a viscous drag on the adjacent layer.

b) The viscous flow is associated with a net transfer of momentum from a more rapidly moving layer to the more slowly moving layer.

Differences:

In a gas, the momentum is transferred by the actual flights of molecules between the layers (intermolecular collisions).

In a liquid, the momentum transfer is due to intermolecular attractive forces between the molecules, which cause a frictional drag between the moving layers.

The viscosity of ***gases increases*** with temperature. The average speed of molecules increases and therefore the probability of collisions increases.

The viscosity of a ***liquid decreases*** with increasing temperature. The reciprocal of the viscosity, the fluidity, can be expressed by an Arrhenius-type expression.

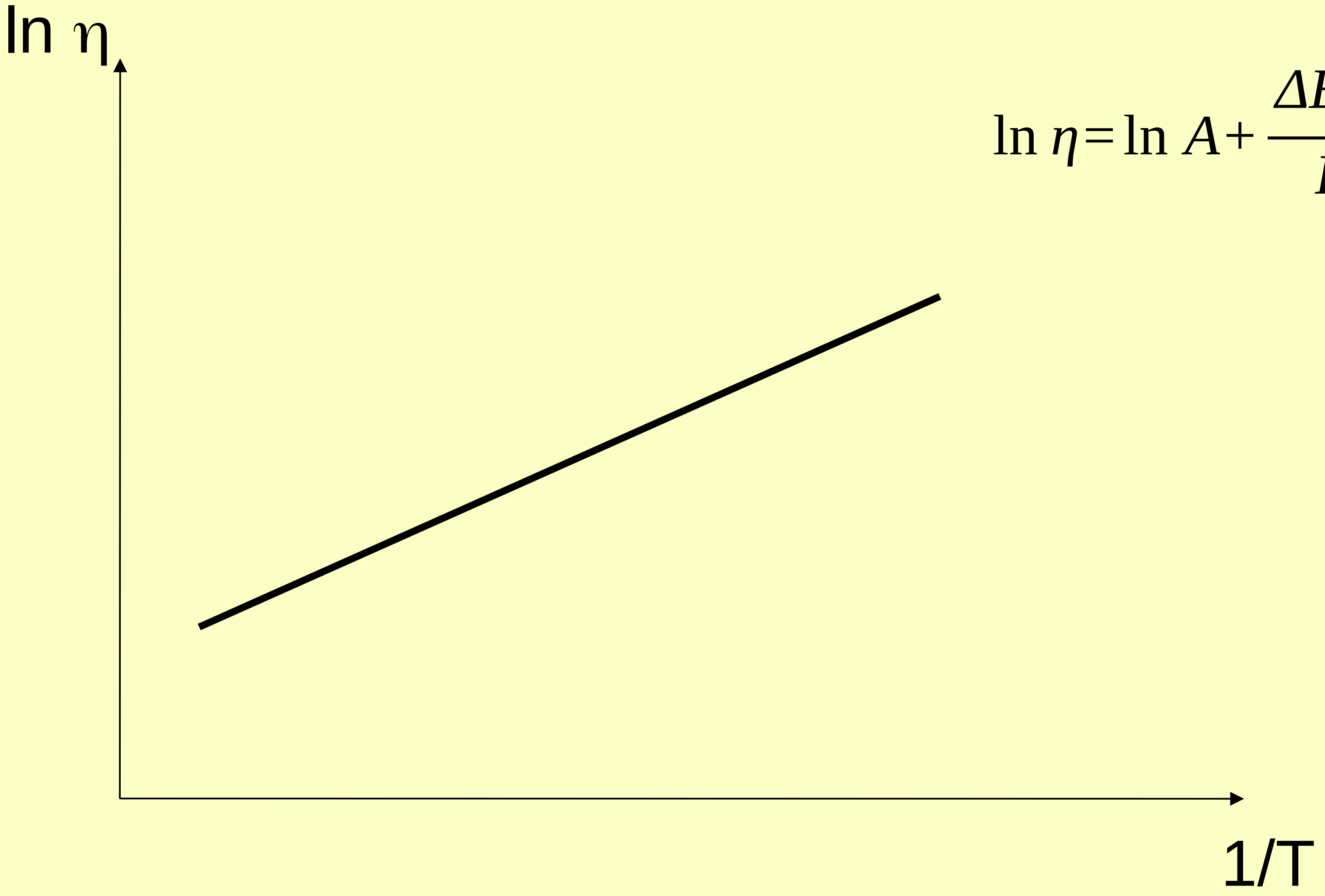
$$\frac{1}{\eta} = B \cdot \exp\left(\frac{-\Delta E_{vis}}{RT}\right) \qquad \text{(T14)}$$

where ΔE_{vis} and B are constants. ΔE_{vis} is the activation energy of the rate process of viscous flow.

The reciprocal of T14 is

$$\eta = A \cdot \exp\left(\frac{\Delta E_{vis}}{RT}\right) \qquad \text{(T15)}$$

The logarithm of viscosity is a linear function of the reciprocal of the temperature:



$$\ln \eta = \ln A + \frac{\Delta E_{vis}}{R} \times \frac{1}{T}$$

Summary

We have discussed three types of transport. Notice the similarity of the equations for the fluxes:

Material	$j_n = -D \cdot \frac{dc}{dx}$	Diffusion	(T4)
Internal energy	$j_q = -\lambda \cdot \frac{dT}{dx}$	Heat conduction	(T10a)
Momentum	$j_p = -\eta \cdot \frac{dv_x}{dy}$	Viscosity	(T13)