ENVIRONMENTAL PHYSICAL CHEMISTRY

EM-LM Chemical Innovation and regulation – Faro 24-28 Feb. 2014

Contents.

Nature and features of transport processes. Frictional coefficient.

Sedimentation, Stokes' law, dynamic and kinematic viscosities, Reynolds number. Conductance and conductivity. Salinity.

Mass balance. Input, output and reaction-terminated flows. Differential balance for individual components.

Molecular and turbulent diffusion. Fick's laws. Factors influencing diffusivity. Atmospheric stability. Pasquill's model for chimney plumes; estimation of effective plume height and ground pollutant concentrations as a function of various parameters. Computer simulations.

Energy balance. Bernoulli's equation for both incompressible fluids and gases. Decrease in atmospheric pressure and temperature with altitude.

Thermal energy. Transport through thermal conduction, convection and irradiation (Stefan-Boltzmann and Wien laws). Greenhouse effect.

Appendix – Common kinetic equations, Arrhenius' law. Biochemical oxygen demand (BOD). Enzymatic catalysis.

Text books – Transparencies used for the lectures (available in pdf format on the site http://emmcchir.org/ChIRM), mainly taken from:

- R. Francesconi, *Appunti di Chimica Fisica Ambientale*, CLUEB, BO, 2002.
- P.A. Vesilind, J.J. Pierce, R.F. Weine, *Environmental Engine-ering*, 3rd Edit., Butterworth-Heinemann, Boston, 1994: Chap. 19.
- D. Eisenberg, D. Crothers, *Physical Chemistry,* The Benjamin/Cummings Publ. Co., 1979: Chap. 15.

TRANSPORT PROCESSES

Transport processes involve a flow of matter. When a particle is subject to a force (F), from random motions a net motion along a direction emerges, thus generating a ***flux*** (particles per unit time and surface), that is, a ***transport process***. Among these, sedimentation (gravitational or centrifugal force), conductance (electrostatic forces) and diffusion, (caused by a concentration, i.e., chemical potential, gradient).

In general, $dU = -F\,dx$, where U is a potential energy and x is a distance. In the absence of a frictional resistance provided by the solvent, the velocity of a particle subject to a constant force would continuously increase. The force F is opposed to the frictional resistance $f\mathbf{v}$ (where f is called the ***frictional coefficient*** ≡ *mass*/*t* and $\mathbf{v}$ is the transport velocity), a force linearly proportional to the velocity which acts in the opposite direction. In a very short time (of the order of magnitude of 10^{-12}-10^{-13} s in solution), the resulting net force becomes null and a maximum (and constant) speed is reached ($d\mathbf{v}/dt = 0$):

$F - f\mathbf{v} = 0$ where $\mathbf{v} = F/f$ is the transport velocity.

N.B. – The transport velocity does not coincide with the absolute velocity, but is the net velocity along a preferential direction (generally much smaller than the absolute speed).

SEDIMENTATION

Sedimentation is the tendency for particles in suspension to settle out of a fluid and accumulate because of the presence of a force field, typically associated with a gravitational force (*gravitational sedimentation*) or a centrifugal force (*centrifugal sedimentation*).

Gravitational sedimentation - This is a mechanical method for separating the various phases which form an emulsion or a suspension, based on the spontaneous process caused by the gravitational force. Therefore, the higher the particle density is (relative to the medium) the more effective is sedimentation. Besides, the sedimentation velocity is also affected by the particle size: the smaller they are, the lower is their sedimentation velocity.

Gravitational sedimentation involves three forces: gravitational force (F_g), against which act Archimedes' force (F_A) and the frictional resistive force ($F_R = f\,v$) of the fluid.

$$F_g - F_A - f\,v = 0$$

where $F_g = m\,g = \rho\,V\,g$ (ρ = *particle density,* and g = *gravitational acceleration* = $9.81\ m\ s^{-2}$)

$$F_A = \rho_m\,V\,g \quad (\rho_m = \textit{density of the medium})$$

$$\Rightarrow \quad (\rho - \rho_m)\,V\,g - f\,v = 0$$

$$\Rightarrow \quad \boldsymbol{v = (\rho - \rho_m)\,V\,g\,/\,f}$$

The resistive force ($f\,v$) is proportional to the sedimentation velocity, the proportionality constant being the frictional coefficient f.

For a spherical particle moving in a viscous fluid with laminar regime and *Reynolds number* < 1 (see following slides), the frictional coefficient f is defined by **STOKES' law**. The more viscous the fluid, the lower the velocity of a sphere falling through gravity :

$\boldsymbol{f = 6\,\pi\,\eta\,r} \quad \Rightarrow \quad F_R = f\,v = 6\,\pi\,\eta\,r\,v$

(η = *viscosity coefficient*, r = *sphere radius*).

$\Rightarrow \quad v = (\rho - \rho_m)\,V\,g\,/\,f = (\rho - \rho_m)\,V\,g\,/\,6\,\pi\,\eta\,r =$

$= (\rho - \rho_m)\,g\,4/3\,\pi\,r^3\,/\,6\,\pi\,\eta\,r \Rightarrow$

$$\boxed{v = \frac{2(\rho - \rho_m)\,g\,r^2}{9\eta}}$$

N.B. – The quadratic dependence of the velocity upon the radius also holds for rain drops falling in the atmosphere. The micro-drops small enough to penetrate into the lungs, because of their low velocity, remain longer in contact with the atmosphere, thus accumulating larger concentrations of pollutants.

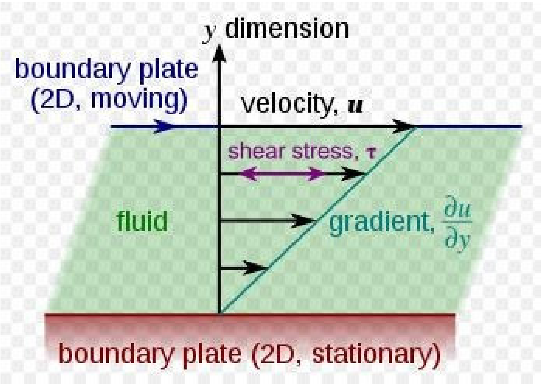
VISCOSITY

Viscosity is a property of fluids which indicates their resistance to flow (or deformation) by ***shear stress*** (or ***tensile stress***). Viscosity is due to friction between neighboring parcels of the fluid that are moving at different velocities. It depends on the nature of the fluid and temperature. It is usually designated with the Greek letter η (*eta*).

In liquids viscosity decreases with increasing temperature, in contrast with gases.

DYNAMIC VISCOSITY

From a mathematical point of view, it is possible to evaluate the force (per unit surface) necessary for modifying the velocity of a small layer of fluid relative to that of another layer at a fixed distance (*h*)



Representation of the shear stress acting on a fluid.

$$\frac{F}{S}=\eta\left(\frac{d\,v}{d\,h}\right)$$

where :

F, *force applied to the measurement planes*
η, *frictional coefficient, called "viscosity"*
dv, *velocity difference between two layers*
dh, *distance between two layers*
S, *surface area of contact between the layers*

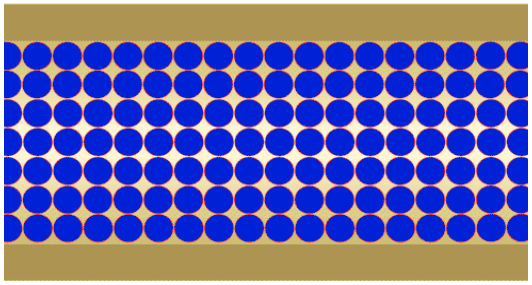
The above equation, attributed to Isaac Newton, describes an ***ideal viscous behaviour***, characterized by a value of the viscosity coefficient η **independent** from both the shear stress (F/S) and velocity gradient (dv/dh, ***shear rate***) .

In fact, for most fluids the viscosity coefficient η is not constant (*non-newtonian fluids*). In any case, the greater the viscosity, the geater the force required to maintain a given velocity gradient.

Viscosity represents a measure of the *cohesion* of the fluid: for instance, glass (which does not possess a definite melting point and a crystalline structure) may be seen as a fluid with very high viscosity.

A fluid with null viscosity ($\eta = 0$) and a density which remains constant with increasing pressure (incompressibile fluid), is called an ideal fluid.

A flux is called ***laminar*** when a fluid flows with infinitesimal layers sliding easily over each other without any mixing, even on a microscopic scale. Such a flux is governed by viscous forces and remains constant over time.



DIMENSIONS and UNITS

The dimensions of viscosity are ***pressure x time***; in the International System its units are *Pascal x second*, ***Pa s***.

In terms of fundamental quantities, its dimensions are *mass* . L^{-1}. t^{-1} (*mass* over *length* and *time*)

$$\Rightarrow\ 1\ Pa\ s = 1\ kg\ m^{-1}\ s^{-1}$$

The unit *poise* (*P*), which belongs to the *c g s* system, is still in use $\Rightarrow$ 1 *poise* = 1 $g\ cm^{-1}\ s^{-1}$.

The following relationships hold: 1 *Pa s* = 10 *P* = 1000 *cP* where *1 cP* (*centipoise*) corresponds to *1 mPa s* *(millipascal s)*. The viscosity of water at room temperature is about 1 *cP* (1,001 *cP* at 20 °C).

KINEMATIC VISCOSITY

The ***kinematic viscosity*** is defined as the ratio between the ***dynamic viscosity*** of a fluid and its ***density***. It measures the extent of the resistance to flow of a fluid current upon the influence of gravity, this tendency depending on both the absolute (dynamic) viscosity and the specific weight of the fluid. For instance, the dynamic viscosity of mercury is 1.7 times larger than that of water, but because of its high specific weight (13.6 g/cm^3) it flows much more rapidly through an aperture. In fact, the kinematic viscosity of mercury is about eight times smaller than that of water at room temperature.

The kinematic viscosity is the ratio between the dynamic viscosity and the density, so that its dimensions are $[mass\ L^{-1}\ t^{-1} \times L^3 / mass] \equiv L^2/t$, where L is a length and t a time. As a unit of measure for the kinematic viscosity the *cgs* unit ***stokes*** (***St*** = 1 cm^2/s) is still generally used (compare below with the diffusion coefficient). In the International System of Units, the kinematic viscosity is measured in $m^2\,s^{-1}$, which corresponds to 10^4 *St*.

REYNOLDS NUMBER

Reynolds number (***Re***) is an adimensional parameter, commonly used in *fluid dynamics*, proportional to the ratio between inertial and viscous forces. *Reynolds* observed that the dynamics of a fluid could be described by combining the average velocity (u), the tube diameter (d) and the kinematic viscosity (v) in a single adimensional factor ($\equiv L\,t^{-1}.\ L\,/\,L^2\,t^{-1}$), defined as :

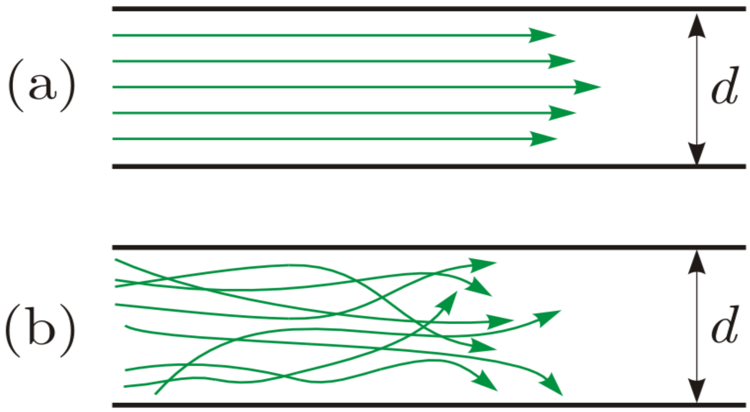
$$Re = u\,d\,/\,v$$

The experiment was carried out with a straight transparent pipe and a fluid with constant flow, where a colorant was injected. Reynolds identified three different types of flows:

- for *Re* values ≤ 2000 the flux remains stationary, as if formed of thin layers interacting only through shear stress (***laminar flow***). The colorant injected in the flow moves along a thin line which remains parallel to the pipe direction.

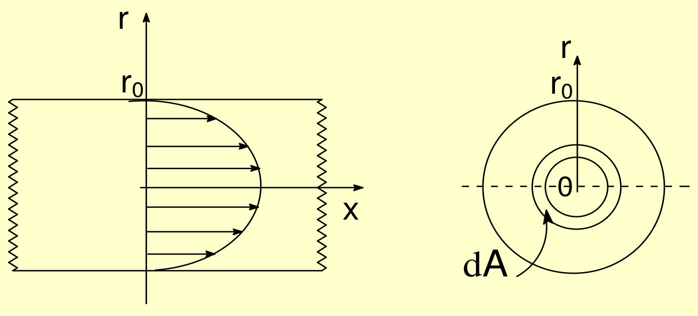
- for values in the 2000 ≤ *Re* ≤ 3000 range the colored line loses its stationary nature and forms small waves, but still remains narrow (***transitional flow***).

- for *Re* values ≥ 3000, the fluctuations increase and the colorant tends to diffuse in the flow (***turbulent flow***), with non-stationary and random motion in all three directions.



Representations of laminar (a) and turbulent (b) flows inside a cylindrical pipe.

EXERCISE **-** Calculate the **average velocity** in a pipe for a viscous liquid with laminar flow (parabolic profile).



Data.
The velocity of the fluid varies with the radius:
$v = C\,(r_o{}^2 - r^2)$.

At the centre, where $r = 0$, $v_{max} = C\,r_o{}^2$

Average velocity $<v>$ over the surface A

(where $A = \pi\, r^2 \quad \Rightarrow \quad dA = 2\pi\, r\, dr$) :

$$< v > \; = \frac{\int_A v\,dA}{\int_A dA} = \frac{\int_A v\,dA}{A}$$

$$< v > = \frac{1}{\pi\, r_o^2}\; 2\pi\, C\, (r_o^2 \int_o^{r_o} r\, d\, r - \int_o^{r_o} r^3\, d\, r) =$$

$$= \frac{1}{r_o^2}\; 2C\; (r_o^2 \times \frac{1}{2}\, r_o - \frac{1}{4}\, r_o^4) \; =$$

$$\Rightarrow \qquad \boxed{< v > = \frac{1}{2}\, C\, r_o^2}$$

N.B. : **$<v> = ½\, v_{\mathrm{max}}$**

CONDUCTANCE and CONDUCTIVITY

The force involved in the transport process ***conductance*** (formerly designated with the historical term *conducibility*) is of an electrostatic nature. The relationships reported below therefore hold, where U is the potential energy.

$$m\frac{dv}{dt} = F - f\,v = 0 \qquad F = -\frac{dU}{dr}$$

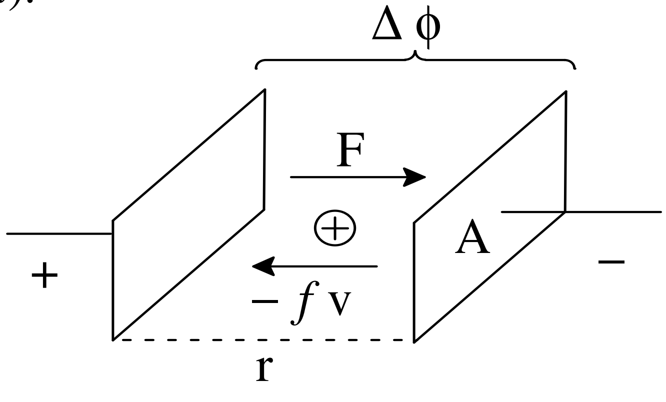
$$U = \frac{q \cdot q'}{r} \quad \Rightarrow \quad F = \frac{q \cdot q'}{r^2}$$

$$\Delta\phi = \frac{U}{q'} = \frac{q}{r}$$

$$E^* = -\frac{d\,\Delta\phi}{dr} = \frac{F}{q'} = \frac{q}{r^2}$$

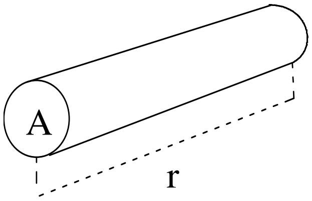
and therefore: $F = E^* . q$; $U = \Delta\phi . q$

A ***potential difference*** ($\Delta\phi \equiv$ *Coulomb/meter* $\equiv$ *Volt*) associated with an ***electric field*** ($E^* \equiv$ *Volt /meter*) is applied to the electrods of the cell of the conductivity meter. A charged particle thus experiences a force F ($\equiv$ *Newton*).



Ohm's law : the current intensity i ($\equiv$ *Coulomb* s^{-1} $\equiv$ *Ampere*) is proportional to $\Delta\phi$ ($\equiv$ *Volt*) and in inversely proportional to the resistance R ($\equiv$ *Ohm*).

$$R = \frac{\Delta\phi}{i}$$



The resistance is proportional to the length (r) and inversely proportional to the cross-section area (A): $R \,.\, A / r$ ($\equiv$ *Ohm cm*) is thus the ***specific resistance***, that is, the resistance normalized per unit length and surface.

The current i is proportional to the surface area A and to the electric field E^* ($= \Delta\phi / r$)

$$\Rightarrow \qquad i = k\,A\,E^* = k\,A\,\Delta\phi / r$$

$$\boxed{k = \frac{i}{\Delta\phi}\,\frac{r}{A} = \frac{1}{R}\,\frac{r}{A}\;(\equiv ohm^{-1}\,cm^{-1})}$$

The proportionality constant ***k*** is the inverse of the specific resistance and is called ***conductivity*** (*specific conducibility*, according to the old terminology).

The conductivity ($\equiv$ *Ohm*$^{-1}$ *cm*$^{-1}$ $\equiv$ *Siemens cm*$^{-1}$) is the conductance normalized per unit surface area and distance between the electrodes of the cell, while the conductance (*Ohm*$^{-1}$ $\equiv$ *Siemens*) is simply the inverse of the resistance ($1/R = i / \Delta\phi$).

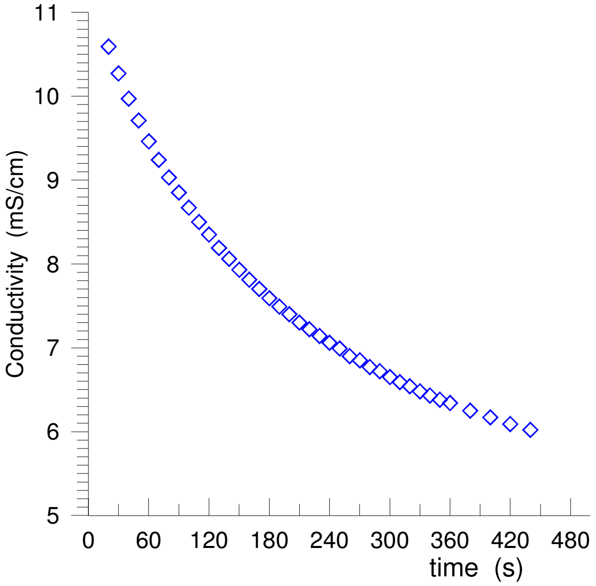
When the conductor is a solution, its conductivity (proportional to the current intensity) is proportional to the ion concentration. The ***ionic equivalent conductivity*** ($\equiv$ $Ohm^{-1}\ cm^{-1}/equiv\ cm^{-3} \equiv Ohm^{-1}\ cm^{2}\ equiv^{-1}$) is the conductivity normalized for the concentration of charges ($equivalents\ cm^{-3}$). In addition, the equivalent conductivity (other factors being equal) varies between different ionic species because of their different frictional coefficients f which determine different transport velocities. Each charged species is characterised by its ***mobility*** (u):

$\mathbf{v} = F/f = E^* q/f = E^* u$ where $u = q/f$ *is the* mobility.

As an example, the reaction

$CH_3COOEt + Na^+ OH^- \rightarrow CH_3COO^- Na^+ + EtOH$

can be easily followed by measuring the conductivity as a function of time. Even though the reaction does not change the number of charged species, the equivalent conductivity (42 $S\ cm^2\ eq^{-1}$) of the acetate anion is sizeably smaller than that (198 $S\ cm^2\ eq^{-1}$) of the (smaller) hydroxyl anion, thus causing a reduction of the conductivity with the degree of completion of the reaction.



SALINITY

Salinity is the content of dissolved salts in a body of water. This parameter is therefore correlated with conductivity. Although in the past salinity was expressed as *chlorinity*, namely, the total content in chlorides (Cl^-), bromides (Br^-) and iodides (I^-), salinity is now measured on the basis of electrical conductivity, thus accounting for all the salts present in solution.

The technical term used to indicate the salt content in the ocean is ***halinity***, because halides (in particular Cl^-) are the most abundant anions dissolved in sea water. Halinity is traditionallly expressed as parts per thousand (*ppt* or *‰*). Considering the density (1.03 *kg/L*) of sea water, approximately equal to one, halinity corresponds to grams of salts per liter of solution.

MASS BALANCE

To make a mass (m) balance, one has to:

1) assign a control volume (V);
2) define a time interval (t) over which the balance has to be performed;
3) define the units of measurement for each quantity (V, t, m, …).

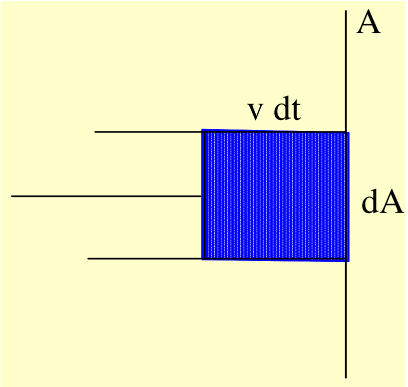
The (differential) equation for the **MASS FLOW RATE** ($\omega \equiv m/t$) is :

$$\omega = dm/dt = \mathrm{Ac} = \mathrm{En} - \mathrm{Ex} + \mathrm{Cr}$$

(**Ac**cumulation = **En**trance − **Ex**it + **Cr**eation)

The term Cr derives from the presence of chemical reactions. For the total mass Cr = 0, but for a single component (k) → $\mathrm{Cr}_k = \nu_k\, r\, V\, M_k \neq 0$,

where: $r = dC/dt$ = **reaction rate** for a species with stoichiom. coeff. = 1, C = concentration, M_k= molecular mass, ν_k = stoichiom. coeff. (for products: $\nu > 0$, for reagents: $\nu < 0$). The following relationships are well known: $C = n/V$; $\rho = m/V$; $m = n\,M = \rho\,V$.



Accumulation of the k component in the control volume V is given:

- by the moles which enter and exit from surface A permeable *to* k ;
- by the chemical reactions that produce or consume k.

The **VOLUMETRIC FLOW RATE** ($\Psi = dV/dt$) is

$\Psi = dV/dt = A\,.\,dx/dt = A\,.\,\mathrm{v}$ (with <u>v = const.</u>)

When the velocity v is not constant over the whole surface A: $\Psi = \int_A \mathrm{v}\, dA$

The **MASS FLOW RATE for a SINGLE COMPONENT *k*** is

$\omega_k = \rho_k\,\Psi = \int_A \rho_k\, \mathrm{v}_k\, dA$ (v_k is perpendicular to dA)

If the **average velocity** ($\langle \mathrm{v} \rangle = \int_A \mathrm{v}\, dA / A$) is available:

$\Psi = \langle \mathrm{v} \rangle A \rightarrow \boldsymbol{\omega_k = \rho_k\, \Psi = \rho_k \langle \mathrm{v}_k \rangle A}$ **(eq. 1)**

In the presence of reactions, the ***mass balance*** for the ***component k*** becomes:

$\mathrm{Ac}_k = dm_k/dt = \omega_k^{En} - \omega_k^{Ex} + M_k\, dn_k^{reaz}/dt$

or $\boldsymbol{\mathrm{Ac}_k = \omega_k = \omega_k^{\mathrm{En}} - \omega_{\mathrm{k}}^{\mathrm{Ex}} + M_k\, V\, \Sigma_j\, \nu_{j,k}\, r_j}$ **(eq. 2)**

(where $r = dC/dt$).

In contrast, for the <u>total mass balance</u> the reaction term is always = 0, because $\Sigma_k\, \nu_k M_{\mathrm{k}} = 0$, that is, the total mass of reagents and products must be equal.

$\Rightarrow \quad \mathrm{Ac} = dm/dt = \omega^{\mathrm{En}} - \omega^{\mathrm{Ex}}$ (total mass)

MOLE FLOW RATE : $\Phi \equiv n/t$

Recalling that $n_k = m_k/M_k$ and $C_k = \rho_k/M_k$, dividing by M_k the above equations (1) and (2) obtained for ω_k, the corresponding relationships are obtained:

$\Phi_\kappa = dn_k/dt = C_k\,\Psi = C_k \langle \mathrm{v}_{\mathrm{k}} \rangle A$ and

$\Phi_\kappa = \Phi_k^{\mathrm{En}} - \Phi_k^{\mathrm{Us}} + dn_k^{\mathrm{reaz}}/dt = \Phi_k^{\mathrm{En}} - \Phi_k^{\mathrm{Ex}} + V\, \Sigma_j\, \nu_{j,k}\, r_j$

N.B. At variance with the total mass, the occurrence of chemical reactions can vary the number of total moles.

- Provided that reactions do not cause volume changes (V= const.): $dV/dt = \Psi^{En} - \Psi^{Ex} = 0 \quad \Rightarrow \quad \Psi^{En} = \Psi^{Ex}$
In this case, denoting with A and A' the entrance and exit apertures of a ***pipe*** :

$$< \mathrm{v} > A = < \mathrm{v}' > A' = \text{const.} \quad (\textit{Castelli's law})$$

- In some cases the balances are simplified, such as for a **STATIONARY SYSTEM** (where all quantities remain constant over time) :

$$dn_k/dt = \Phi^{En} - \Phi^{Ex} + V\,\Sigma_j\,\nu_{j,k}\,r_j = 0$$

$$\Rightarrow \qquad \boldsymbol{\Phi_k^{Ex} - \Phi_k^{En} = V\,\Sigma_j\,\nu_{j,k}\,r_j}$$

with $\Psi^{En} = \Psi^{Us}$, recalling that $\Phi_k = C_k <\mathrm{v}_k> A = C_k\,\Psi$, dividing by Ψ one obtains :

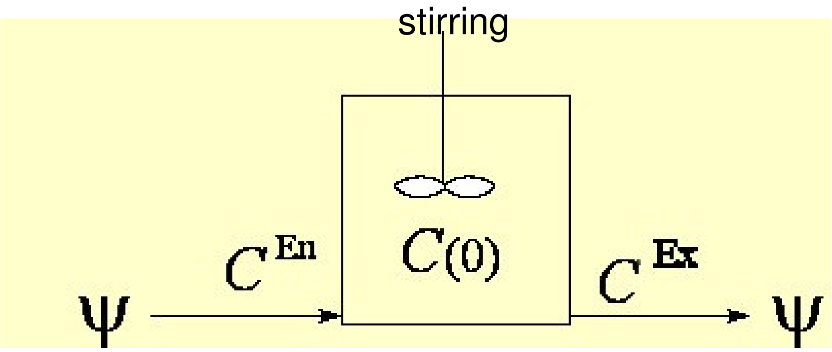
$$\boldsymbol{C_k^{Ex} - C_k^{En}} = (V/\Psi)\,\Sigma_j\,\nu_{j,k}\,r_j = \boldsymbol{\theta\,.\,\Sigma_j\,\nu_{j,k}\,r_j}$$

where $\boldsymbol{\theta}$ (= V/Ψ) is the ***average permanence time*** in volume V.

N.B. This equation defines a relationship, under steady state conditions, between the concentrations entering and leaving the control volume provided we can express $\boldsymbol{r_j}$ as a function of $\boldsymbol{C_k^{Ex}}$ (= $\boldsymbol{C_k}$ in the control volume), namely, if we know the kinetic equations.

Note also that when k is a reagent both the difference $\boldsymbol{C_k^{Ex} - C_k^{En}}$ and $\boldsymbol{\nu_{j,k}}$ are negative.

REMOVAL OF POLLUTANTS IN LIQUID PHASE



The concentration in the reactor is assumed to be uniform and equal to C^{Ex}. At $t = 0$ the concentration is $C(0)$.

Mole balance, under steady state conditions with

$\Phi = C\,\Psi$ and $\Psi^{En} = \Psi^{Ex}$:

$dn/dt = \Phi_k^{En} - \Phi_k^{Ex} + V\ \Sigma_j\, \nu_{j,k}\, r_j = 0$

dividing by Ψ → $C_k^{Ex} - C_k^{En} = \theta\,.\,\Sigma_j\, \nu_{j,k}\, r_j$

where $\theta = V/\Psi$ is the **average permanence time**.

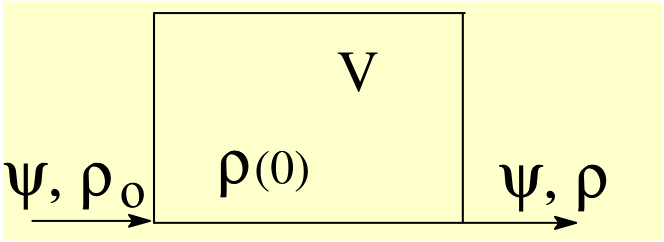
If k is a reagent involved in a single first-order reaction

$\Rightarrow\ \nu = -1\ ;\ r = dC^{reaz}/dt = K\,C$, where $C = C^{Ex}$:

$C_k^{Ex} - C_k^{En} = -\,\theta\, K\, C_k^{Ex} \quad \Rightarrow \quad \boxed{C_k^{Ex} = \frac{C_k^{En}}{1+K\theta}}$

N.B. – C(0), the concentration at $t = 0$, does not influence the final value of C_k^{Ex}, but only the time required to reach the steady state conditions.

BASIN REMEDIATION



The water of a 15000 m^3 pond contains a toxic pollutant of density ρ(0) at time $t = 0$; the basin is fed by a stream with a flow of $\Psi = 1\ m^3/s$ and a constant density (ρ_o) of the pollutant. **No chemical reactions (**and **no** steady state conditions) take place.

Determine 1) the exit density ρ as a function of time and 2) the time required to reduce it by a factor of 100 when the basin is fed with pure water ($\rho_o = 0$).

Because of the absence of reactional terms, the mass balance is simply: $dm/dt = \omega^{En} - \omega^{Ex}$

where $m = V\rho$; $\omega = \Psi.\rho$ $(\Psi^{En} = \Psi^{Ex} = \Psi)$

$\Rightarrow \quad dm/dt = V.\, d\rho/dt = \Psi\,(\rho_o - \rho)$

$\rightarrow \quad d\rho/dt = (\Psi/V)\,(\rho_o - \rho)$

namely: $d\rho\,/(\rho_o - \rho) = dt/\theta$

where $\theta = V/\Psi$ is the average permanence time.

N.B. Analogous to the mole balance shown before,
$dn/dt = V.\, dC/dt = \Phi^{En} - \Phi^{Ex} + V\,\Sigma_j\, \nu_{j,k}\, r_j =$
$\Psi\,(C^{En} - C^{Ex}) + V\,\Sigma_j\, \nu_{j,k}\, r_j$ with no reactions nor steady state conditions $\rightarrow$ $dC/dt = \Psi/V\,(C^{En} - C^{Ex})$

By integration of $d\rho\,/(\rho_o - \rho) = dt/\theta$:

$\ln\,[(\rho_o - \rho)/(\rho_o - \rho(0))] = -\,t\,/\,\theta$

$\rightarrow \quad \rho = \rho_o - (\rho_o - \rho(0))\,.\,e^{-\,t/\theta}$

If the basin is fed with pure water ($\rho_o = 0$) ,

$\rightarrow \quad \boldsymbol{\rho = \rho(0)\,.\,e^{-\,t/\theta}}$

N.B. This result parallels the integrated equation for a first-order kinetic law, where K is replaced by $1/\theta$ (dimensions ≡ t^{-1}).

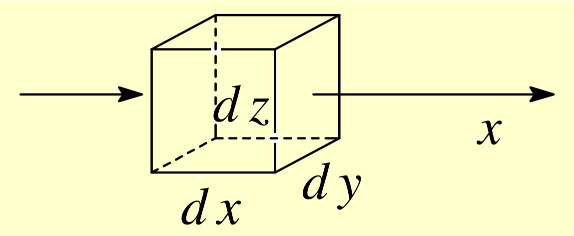
With $\rho\,/\rho(0) = 10^{-2}$

and $\theta = 15000\ m^3/\,1\ m^3\ \mathrm{s}^{-1} = 15000\ s$:

$\ln 10^{-2} = -\,\mathrm{t}/\theta = -\,\mathrm{t}\,/15000\ s$

$t = -\,(15000\ s\,/3600\ s/h\ )\,\ln 10^{-2} = 19.2\ h$

DIFFERENTIAL MASS BALANCE FOR COMPONENT *k*



Consider the mass flow rate through the surfaces perpendicular to the *x* axis (analogous considerations can be made for the other 2 axes).

For component *k* : $\boldsymbol{\omega}^{\mathbf{En}}_{\boldsymbol{k,x}} = \rho_k \, \mathrm{v}_{k,x} A = \rho_k \, \mathrm{v}_{k,x} \; dy \;\; dz$ (where $A = dy \; dz$).

The corresponding flow rate at $x + dx$ will be :

$\boldsymbol{\omega}^{\mathbf{Ex}}_{\boldsymbol{k,(x+dx)}} = \omega^{\mathrm{En}}_{k,x} + (\partial \, \omega_{k,x} / \partial \, x) \; dx$

so that the ***net flow rate*** ω_k along *x* is :

$\omega_{k,x} = \partial \, m_{k,x} / \partial \, t = \omega_k^{\mathrm{En}} - \omega_k^{\mathrm{Ex}} = - (\partial \; \omega_{k,x} / \partial \; x) \; d\,x =$
$= - \, [\partial \, (\rho_k \, \mathrm{v}_{k,x}) / \partial \, x] \; d\,x \;\; d\,y \;\; d\,z$

Recalling that $V = d\,x \, . \, d\,y \, . \, d\,z$:

$\rightarrow \quad \partial \, m_{k,x} / \partial \, t = - \, [\partial \, (\rho_k \, \mathrm{v}_{k,x}) / \partial \, x] \; . \; V$

and that $\rho = m / V \quad \Rightarrow \quad \boldsymbol{\partial \, \rho_k / \partial t = - \, \partial \, (\rho_k \, \mathrm{v}_{k,\,x}) / \partial x}$

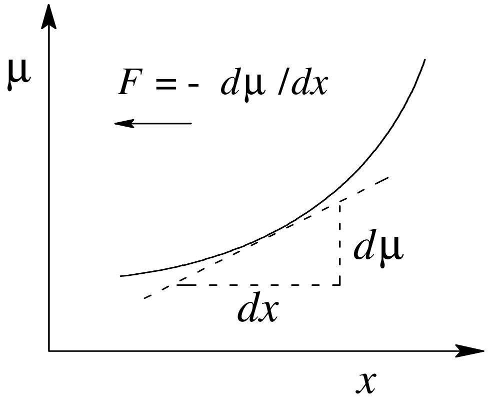
N.B. This important relationship accounts for the convective effect of wind in the differential equation to be solved in Pasquill’s model: when v = const.,

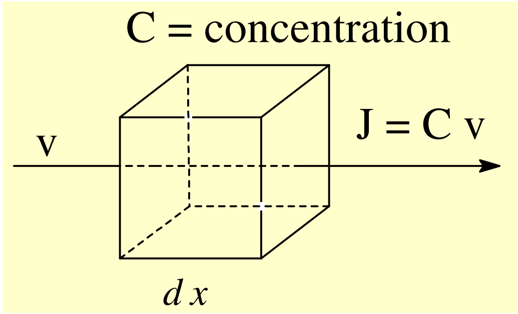
$\partial \, \rho_k / \partial \, t = - \, \mathrm{v}_{k,,x} \, . \, \partial \, \rho_k / \partial \, x$

When reactional terms (not so far considered) are present, the above equation becomes:

$\boldsymbol{\partial \, \rho_k / \partial t = \; - \, \partial \, (\rho_k \, \mathrm{v}_{k,\,x}) / \partial x + M_k \, \Sigma_{\mathrm{j}} \, \nu_{k,\,\mathrm{j}} \, r_{\mathrm{j}}}$

MOLECULAR DIFFUSION





In the case of ***molecular diffusion*** the force F is associated with a concentration gradient, which in turn causes a gradient in the chemical potential (μ), i.e., the potential energy U.

$$\mu = \mu^o + RT \ln C \quad \rightarrow \quad F = - d\mu / dx = - RT\, d \ln C / dx$$

It is to be noted that if μ increases along a direction the force is applied in the opposite direction.

$$F - f v = 0 \qquad \rightarrow \qquad v = F/f \qquad (f \equiv mass/t)$$

For a single molecule: $\mathrm{R} / \mathrm{N_A} = k_B$

$$v = F/(N_A f) = -k_B T/f \,.\, (d \ln C/dx)$$

$$\Rightarrow \qquad v = -\frac{k_B T}{f C} \times \left(\frac{dC}{dx}\right)$$

A **flux** (***J***) is a ***flow rate*** (in number of particles or mass or moles) ***per surface unit***, so that

in terms of <u>mass</u>, $J = \omega / A \qquad (J \equiv mass\ L^{-2}\ t^{-1})$

and, recalling that $\omega = \rho\, v\, A$, $\Rightarrow$ $\boldsymbol{J = \rho v}$

or, in terms of <u>moles</u>, C replaces ρ : $\boldsymbol{J = C v}$

When all particles possess the same velocity v^* a **CONVECTIVE FLUX** (movement of the baricentre of the whole system) occurs.

$J_k = \rho_k v_k$ can be written as $J_k = \rho_k (v_k - v^*) + \rho_k v^*$ where $J_k = \rho_k v^*$ is the contribution of component k to the convective flux, while the non-convective part is defined as **DIFFUSIVE FLUX** : $J_k = \rho_k (v_k - v^*)$

or (moles instead of mass): $J_k = C_k (v_k - v^*)$

When $v^* = 0$ (null velocity of the baricentre)

$\boldsymbol{J_k = C_k v_k}$.

Recalling that $v = - k_B T / (f C) . (dC/dx)$

$J = C v = - k_B T / f . (dC/dx)$ $(J \equiv mol\ cm^{-2}\ s^{-1})$

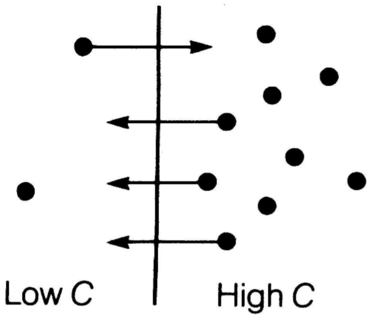
$$\Rightarrow \quad \boxed{J = -D \left(\frac{dC}{dx} \right)_t}$$ ***Fick's 1st Law***

where $\boldsymbol{D} = k_B T / f$ = **DIFFUSION COEFFICIENT** or **DIFFUSIVITY.**

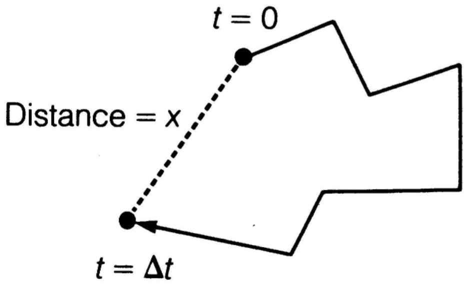
N.B. The minus sign "–" indicates that the flux is positive when the gradient of concentration is negative.

Each molecule follows a random path with a given absolute velocity, but a net movement in a preferential direction (x) takes place with velocity v.

The average space along x as a function of time can be evaluated from ***Einstein's Equation*** : $\boldsymbol{< x^2 > = 2 D . t}$



A high concentration to the right of an imaginary partition produces greater probability for motion to the left than to the right. Each molecule has an equal probability of crossing the partition, but because there are more molecules on the right, the number that move from right to left is greater than the number crossing in the other direction.



Brownian motion of a molecule can be described by a random walk, in which x is the net distance moved in time Δt. From the analysis of the random walk in Section 14-12 we expect that the mean square displacement $\overline{x^2}$ (analogous to the mean square end-to-end distance in a polymer chain) should be proportional to Δt. The exact equation, $\overline{x^2} = 2D\Delta t$, was originally derived by Einstein.

N.B. The dimensions of the diffusion coefficient D are $L^2\, t^{-1}$, the same dimensions of kinematic viscosity.
For macromolecules in solution, the value of D falls within the range 10^{-8}-10^{-6} $cm^2\, s^{-1}$. Under these conditions crossing a living cell (10^{-4} cm) would take about 5 *msec*. [$t = 10^{-8}\ cm^2 / (2 . 10^{-6}\ cm^2\ s^{-1}) = 5 . 10^{-3}\ s$], but about 160 *years* to travel the distance of 1 meter.

However, for gas-phase molecules D (10^{-1}–10 $cm^2\, s^{-1}$ in conditions of ***turbulent diffusion***) is many orders of magnitude larger. Turbulent diffusion occurs in the presence of tangential forces which act as a “stirrer”, thus increasing the diffusion rate.

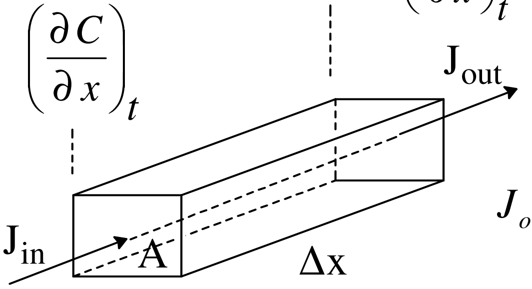
FICK'S 2nd LAW

Fick's 1st law holds at any fixed time, but the concentration gradient is not constant (it decreases with increasing time), so that an additional equation is necessary to describe the evolution of the process. Recalling that $J \equiv mol\, A^{-1} t^{-1}$:

$$\frac{\Delta C}{\Delta t} = \frac{A\left(J_{in} - J_{out}\right)}{\Delta V} = \frac{J_{in} - J_{out}}{\Delta x}$$

$$\left(\frac{\partial C}{\partial x}\right)_t + \Delta\left(\frac{\partial C}{\partial x}\right)_t$$

$$\left(\frac{\partial C}{\partial x}\right)_t$$



$$J_{out} = -D\left[\left(\frac{\partial C}{\partial x}\right)_t + \Delta\left(\frac{\partial C}{\partial x}\right)_t\right]$$

$$J_{in} = -D\left(\frac{\partial C}{\partial x}\right)_t$$

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

By conversion of the Δ limits to derivative :

$$\boxed{\left(\frac{\partial C}{\partial t}\right)_x = D\left(\frac{\partial^2 C}{\partial x^2}\right)_t}$$

Fick's 2nd Law

The concentration change per unit time is proportional to the difference between the entrance and exit fluxes, a relationship which leads to Fick's 2nd Law.

Fick's 2nd Law → MOLECULAR DIFFUSION

$$\left(\frac{\partial C}{\partial t}\right)_x = D\left(\frac{\partial^2 C}{\partial x^2}\right)_t$$

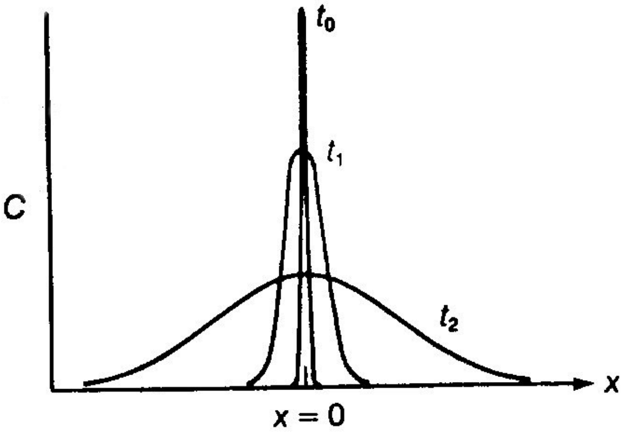
The solution depends on the boundary conditions.

If initially ($t=0$) the whole mass is concentrated on a plane (at $x=0$) and x may take all values from $-\infty$ to $+\infty$, the solution (concentration as a function of x and t) is:

$$\Rightarrow \qquad \boxed{C_{(x,t)} = \frac{C_0}{2\sqrt{\pi D t}}\ exp\left(-\frac{x^2}{4Dt}\right)}$$

The average quadratic distance (Einstein's equation) is obtained from this solution :

$$< x^2 > = \frac{\int_{-\infty}^{+\infty} x^2\, C_{(x)}\, d\,x}{\int_{-\infty}^{+\infty} C_{(x)}\, d\,x} = 2\ D\,t$$



The maximum concentration (***C***) is always found at x = 0, but decreases with time.

At $x \neq 0$, the pre-exponential factor decreases with t, while the exponential factor increases. As a result, ***C*** first increases with time, then reaches a maximum and then decreases. [Verify with simulation software]

Note that D and t have the same effect.

$\partial \rho/\partial t = D\,(\partial^2\rho/\partial x^2) - v_B\,(\partial \rho/\partial x)$

(to be completed with the derivatives relative to axes y e z, and possible reactional terms), where $-v_B\,(\partial\rho/\partial x)$ takes into account the motion of the centre of mass with velocity v_B (convective flux), as seen in slide N. 21).

This is in fact the differential equation to be solved in the **PASQUILL MODEL** for the dispersion of a plume, where a constant-speed wind moves the center of mass (convection) along x, turbulent diffusion operates along the three directions, and the presence of steady state conditions is assumed:

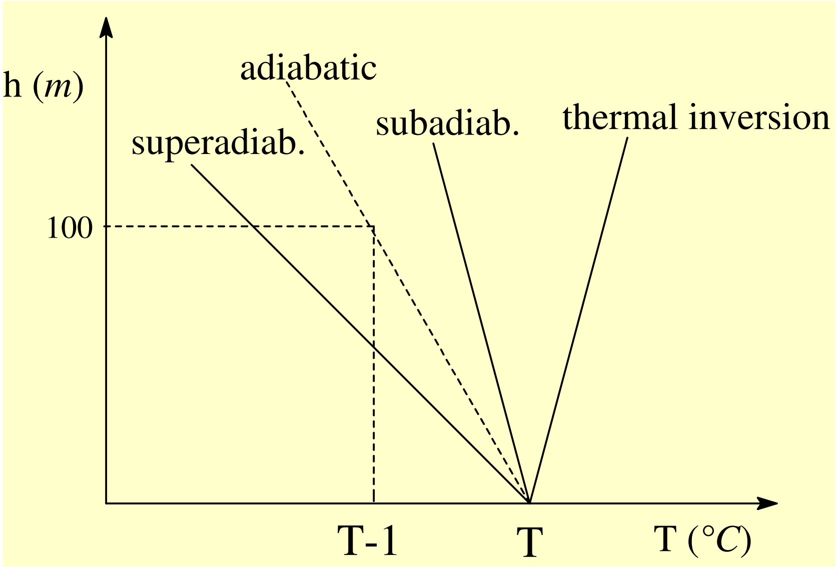
$$\frac{\partial \rho}{\partial t} = D\left(\frac{\partial^2 \rho}{\partial x^2} + \frac{\partial^2 \rho}{\partial y^2} + \frac{\partial^2 \rho}{\partial z^2}\right) - v\,\frac{\partial \rho}{\partial x} = 0$$

N.B. The same equation is also used in other dispersion models (called **Gaussian** dispersion models), for instance, for environmental impact assessments or numerical simulations to predict the extent of salt water intrusion through porous media in coastal areas.

STABILITY OF AIR

The Pasquill model categorizes the atmospheric turbulence into six **stability classes** named A, B, C, D, E and F, with class A being the most unstable (or most turbulent) class, and class F the most stable (or least turbulent) class. The class of stability is determined by the velocity of the temperature decrease of the atmosphere with increasing altitude. An additional class (G) was included to account for thermal inversion.

ADIABATIC COOLING VELOCITY OF DRY AIR
(**dry adiabatic lapse rate**)



The increase of gravitational potential energy is accompanied by a temperature decrease.

$$C_p\, dT = -m\, g\, dh$$

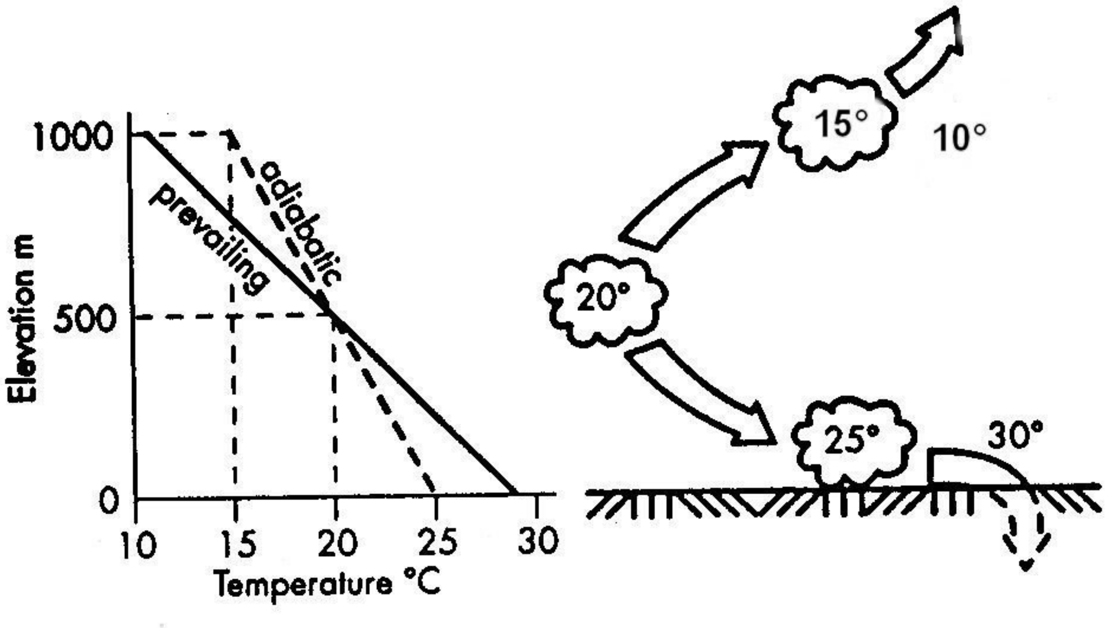
$$\overline{C}_p = 7/2R = 29.1\ \ J\, K^{-1}\, mol^{-1}$$

$$dT/dh = -2.9\times10^{-3}\times9.8/29.1$$

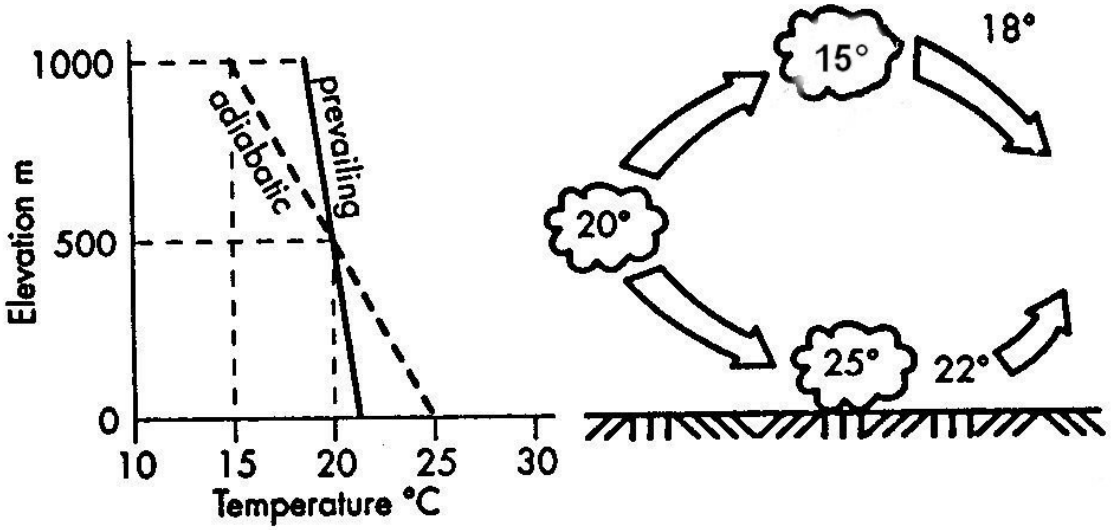
$$dT/dh = -M^{air}\, g/\overline{C}_p$$

$$M^{air} = 29\times10^{-3}\, Kg$$

$$dT/dh \approx -0.01\ K\, m^{-1}$$
$$\approx -1\, K/100\ m$$



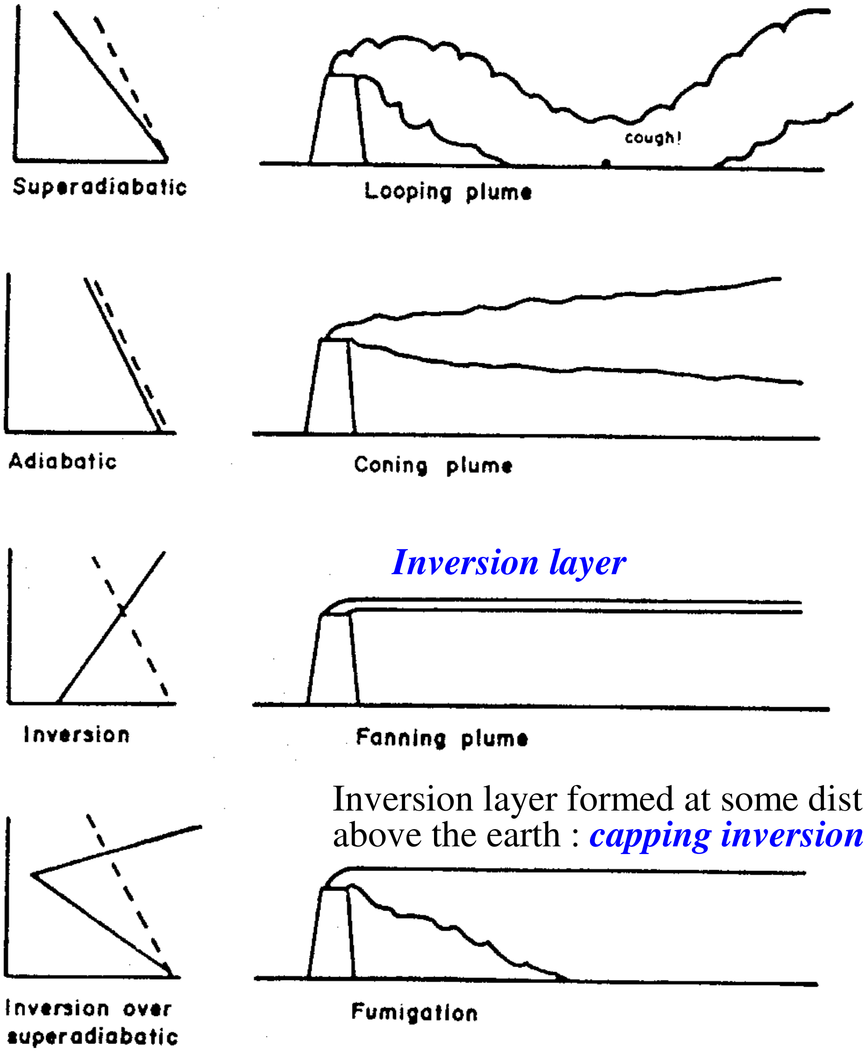
A. Super-adiabatic conditions (unstable)



B. Sub-adiabatic conditions (stable)

Figure 19–9. Stability and vertical air movement.
[from Vesilind et al., Chap. 19]

Plume shape as a function of atmospheric stability



Inversion layer

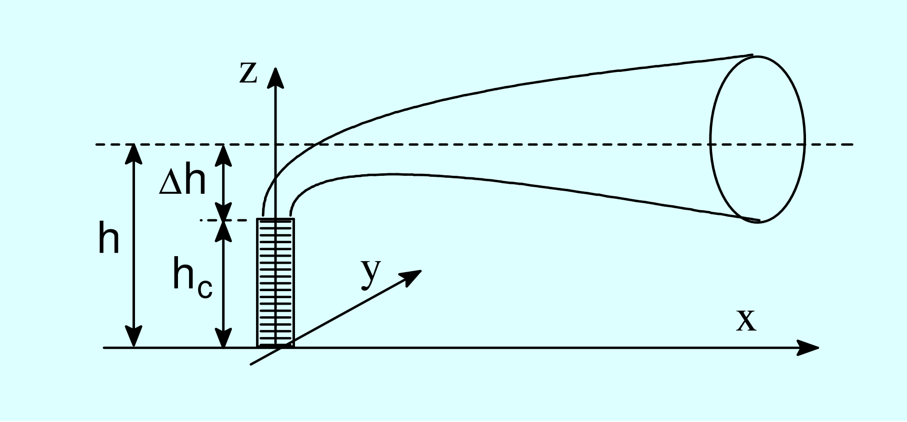
Inversion layer formed at some distance above the earth : ***capping inversion***.

Figure 19–12. Plume shapes and atmospheric stability.

[from Vesilind et al., Chap. 19]

TURBOLENT DIFFUSION

PASQUILL'S MODEL FOR A STACK PLUME



The Figure shows the features of the Gaussian dispersion model, with the geometric arrangement of source (at the origin), wind (along the *x*-axis) and plume. As the plume moves downwind, it spreads laterally (*y*-axis) and vertically (*z*-axis) from the centerline. The pollutant concentrations along the *y*- and *z*-axis have the shape of Gaussian curves.

The gaseous mass emitted continuously from the stack adopts a conical shape under the effects of **turbulent diffusion** along the three directions and **convection** caused by the wind with constant velocity *v* along the *x* direction.

Because stack gases are emitted at temperatures higher than ambient, the buoyant plume will rise some distance before travelling downwind. The sum of this vertical rise and the physical stack height is the effective stack height (h). Thus the zero of the *z*-axis is at ground level, and the plume axis is at z = h.

Assuming stationary state conditions, the differential equation to solve is :

$$\frac{\partial \rho}{\partial t} = D\left(\frac{\partial^2 \rho}{\partial x^2} + \frac{\partial^2 \rho}{\partial y^2} + \frac{\partial^2 \rho}{\partial z^2}\right) - v\,\frac{\partial \rho}{\partial x} = 0$$

An approximate solution (***Pasquill's model***) is:

$$\rho_{(x,y,z)} = \frac{\omega}{2\pi \sigma_y \sigma_z v}\; e^{-\frac{y^2}{2\sigma_y^2}} \left[e^{-\frac{(z-h)^2}{2\sigma_z^2}} + e^{-\frac{(z+h)^2}{2\sigma_z^2}} \right]$$

where: ρ = pollutant density (g/m^3) [N.B.: $\rho = C.\,M$]
ω = velocity of pollutant emission (g/s) ;
v = wind speed along x (m/s) ;
σ_y, σ_z = standard deviations of the plume along the y- and z-axis (m)

This solution consists of a pre-exponential term and Gaussian exponential terms, in analogy with the solution of Fick's second law. Along the x-axis convection is the dominant effect (diffusion can be neglected), while reflection of gaseous pollutants along the z-axis from the surface of the ground are accounted for by the sum of two exponentials. For $z = 0$ the two exponentials are equal, for $z > 0$ the second one becomes rapidly very small. $\boldsymbol{\sigma_y}$ and $\boldsymbol{\sigma_z}$ are functions of x, the distance from the stack.

Of particular interest is the **ground-level concentration** ($z = 0$) with $y = 0$ (that is, below the plume axis) :

$$\rho_{(x,0,0)} = \frac{\omega}{\pi \sigma_y \sigma_z v} e^{-\frac{h^2}{2\sigma_z^2}}$$

Recalling that σ_y and $\sigma_z = f(x)$ and $\sigma_y \approx$ k σ_z, $d\rho / d\sigma_z = 0$ gives the σ_z value corresponding to the **maximum concentration at ground level** :

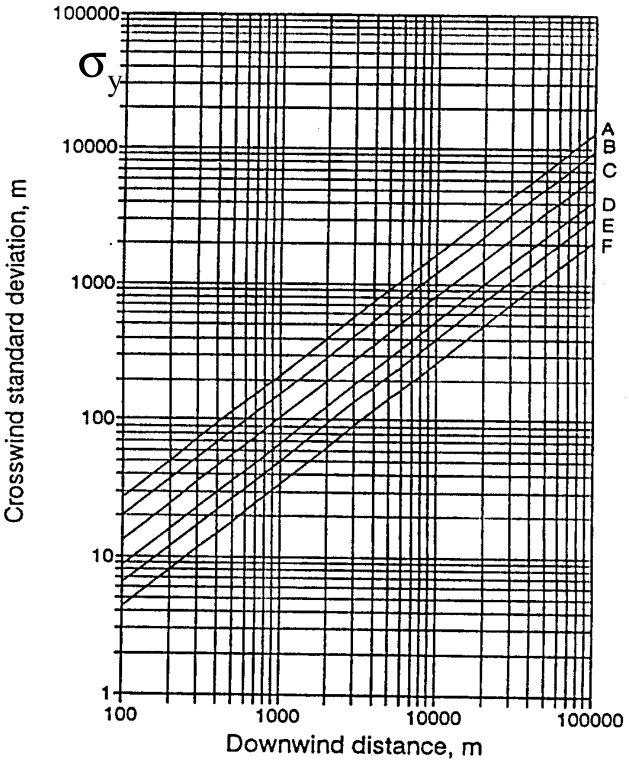
$\sigma_z = \frac{h}{\sqrt{2}}$, which leads to $\rho_{MAX} \approx \frac{2\omega}{\pi v h^2 e}$

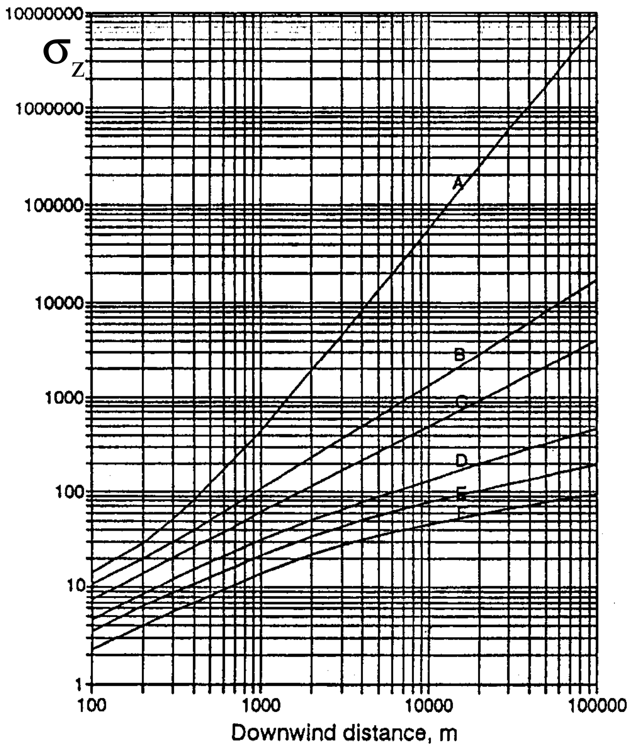
- The distance (x) from the stack which corresponds to $\sigma_z = h/\sqrt{2}$ depends on the stability of the atmosphere: x decreases with increasing super-adiabaticity of the atmosphere. The Pasquill model defines seven classes (A-G) of stability. A-C are super-adiabatic, D is neutral, E and F sub-adiabatic and G indicates thermal inversion.

- $\rho_{MAX} = \frac{2\omega}{\pi v h^2 e}$ shows no dependence upon the stability class, but includes the approximation $\sigma_y = \sigma_z$ while, except for class A, $\sigma_y > \sigma_z$; moreover, the height increase (Δh) increases with super-adiabaticity.

Finally, it is to be noted that ρ_{MAX} at ground level is not the most important factor when evaluating the efficiency of pollutants dispersion.

Dispersion graphs along *y* e *z* as a function of distance and class stability





ATMOSPHERIC STABILITY UNDER VARIOUS CONDITIONS

	DAY: SOLAR RADIATION			NIGHT : CLOUDY	
wind speed (*m/s*)	strong	moderate	slight	**> 50 %**	**< 50%**
< 2	A	A-B	B	E	F
2-3	A-B	B	C	E	F
3-5	B	B-C	C	D	E
5-6	C	C-D	D	D	D
>6	C	D	D	D	D

- The **density at the stack exit** can be calculated from

$$\omega = \rho_{Ex}\, \Psi = \rho_{Ex}\, v_{Ex}\, A = \rho_{Ex}\, v_{Ex}\, \pi\, (d/2)^2$$

once the mass emission flow (ω), the average exit speed (v_{us}) and the diameter (d) are known.

EFFECTIVE PLUME HEIGHT (Vesilind, Chap. 19)

The stack axis is higher than the stack itself. The rise depends, among other factors, on the exit speed of the gas and the heat flow (which determines the buoyancy effect) and can be approximatively evaluated with the equation:

$$\boxed{\Delta h = a\, .V_{Ex}\, .\, d\,/\, v + b\, .\, Q^{0.5}\,/\, v}$$

where

$\Delta h \equiv m$ (plume rise)

$Q \equiv kJ\ s^{-1}$ (emitted heat flow)

$d \equiv m$ (stack diameter)

$V_{Ex} \equiv m\ s^{-1}$ (gas exit speed)

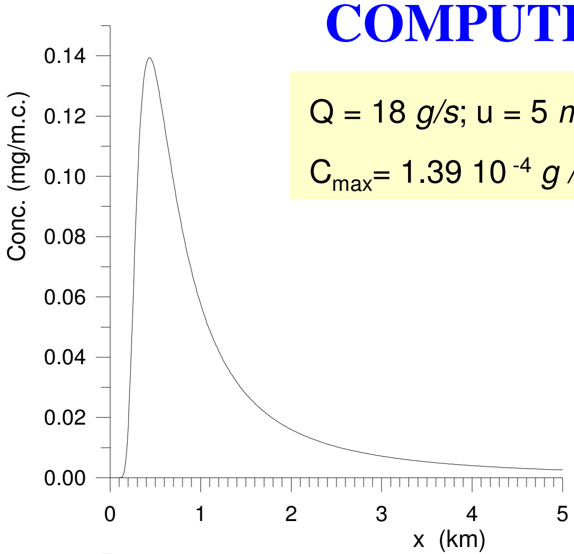
$v \equiv m\ s^{-1}$ (wind speed)

and the coefficients ***a*** e ***b*** are taken from the Table:

Stability class	***a***	***b***
super-adiabatic	3.47	5.15
neutral	0.35	2.64
sub-adiabatic	- 1.04	2.24

The above equation gives a reasonably accurate estimate, although distinguishing only three stability classes. Moreover, it does not account for specific morphological features, for instance, between open country and urban environments.

COMPUTER SIMULATIONS

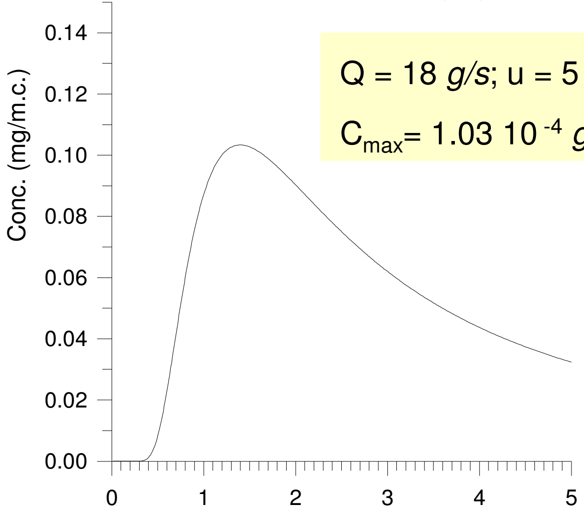


Q = 18 *g/s*; u = 5 *m/s*; H = 60 *m*; stab. class = **B**

C_{max}= 1.39 10^{-4} *g /m*^{3}; x_{max} = 0.43 *km*

Pasquill's model.

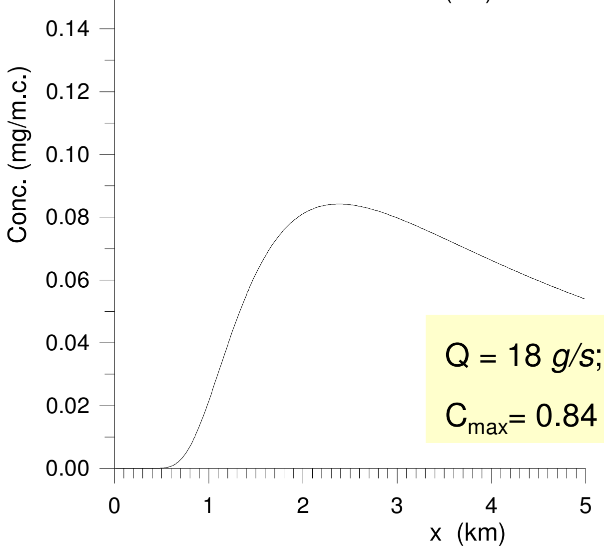
Concentration at ground level as a function of the **stability class**



Q = 18 *g/s*; u = 5 *m/s*; H = 60 *m*; Stab. class = **D**

C_{max}= 1.03 10^{-4} *g /m*^{3}; x_{max} = 1.4 *km*

N.B.: the effect of the stability class has been isolated. In a better approximation, however, the effect of the stability class on the effective height should also be accounted for, thus attenuating (or inverting) the C_{max} differences (see next slide).

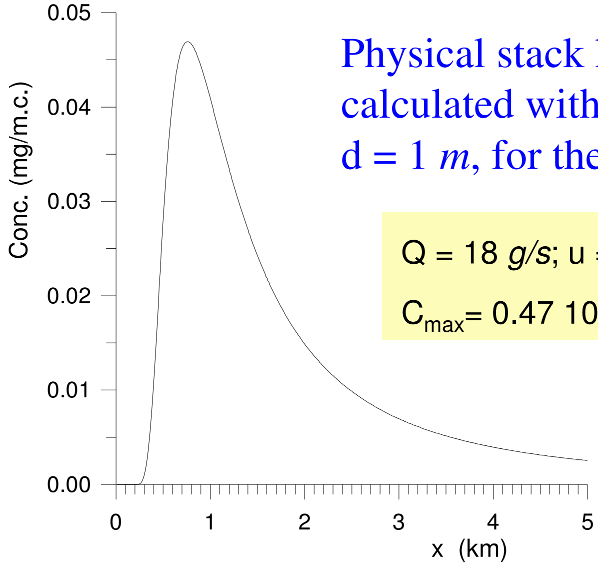


Q = 18 *g/s*; u = 5 *m/s*; H = 60 *m*; Stab. class = **E**

C_{max}= 0.84 10^{-4} *g /m*^{3}; x_{max} = 2.4 *km*

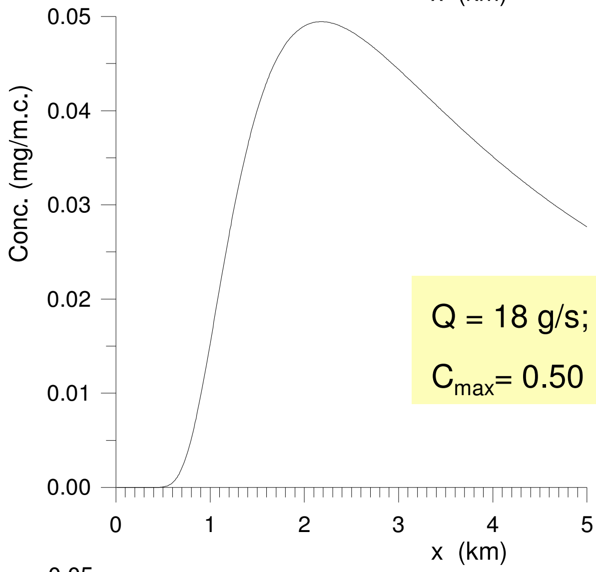
COMPUTER SIMULATIONS

Physical stack height = 60 *m*, and Δh calculated with 2000 *kJ/s*, V^{Ex} = 5 *m/s*, d = 1 *m*, for the various stability classes:



Q = 18 *g/s*; u = 5 *m/s*; **H = 109 *m***; Stab. class = **B**

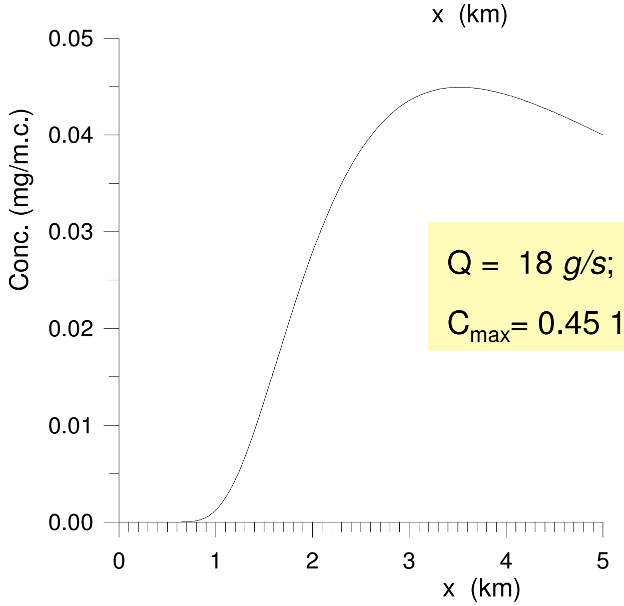
C_{max}= 0.47 10 $^{-4}$ *g /m³*; x_{max} = 0.76 *km*



The physical height being the same, **the effective height decreases with stability.**

Q = 18 g/s; u = 5 m/s; **H = 84 *m***; Stab. clas = **D**

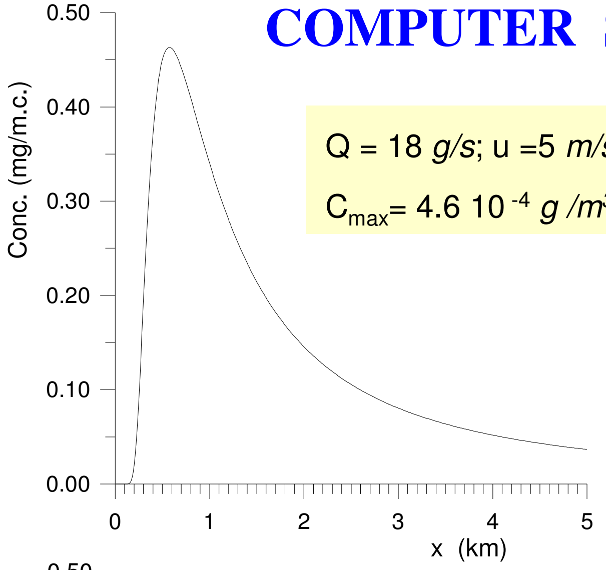
C_{max}= 0.50 10 $^{-4}$ *g /m³*; x_{max} = 2.18 *km*



Q = 18 *g/s*; u = 5 *m/s*; **H = 79 *m***; Stab. class= **E**

C_{max}= 0.45 10 $^{-4}$ *g /m³*; x_{max} = 3.52 *km*

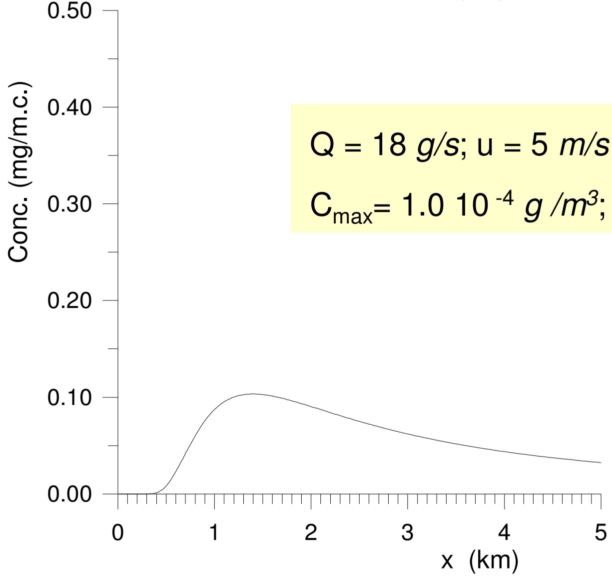
COMPUTER SIMULATIONS



Q = 18 *g/s*; u =5 *m/s*; H = **30** *m*; Stab. class = D

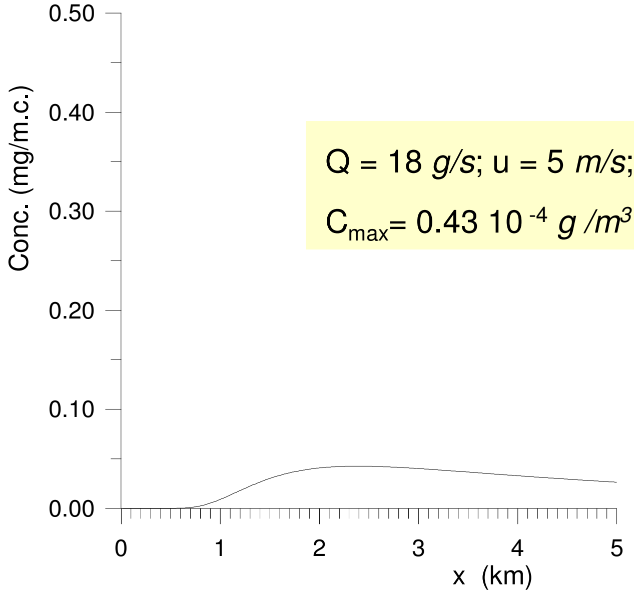
C_{max}= 4.6 10^{-4} g/m^3; x_{max} = 0.6 *km*

Pasquill's model. Concentration at ground level as a function of the **stack height**.



Q = 18 *g/s*; u = 5 *m/s*; H = **60** *m*; Stab. class = D

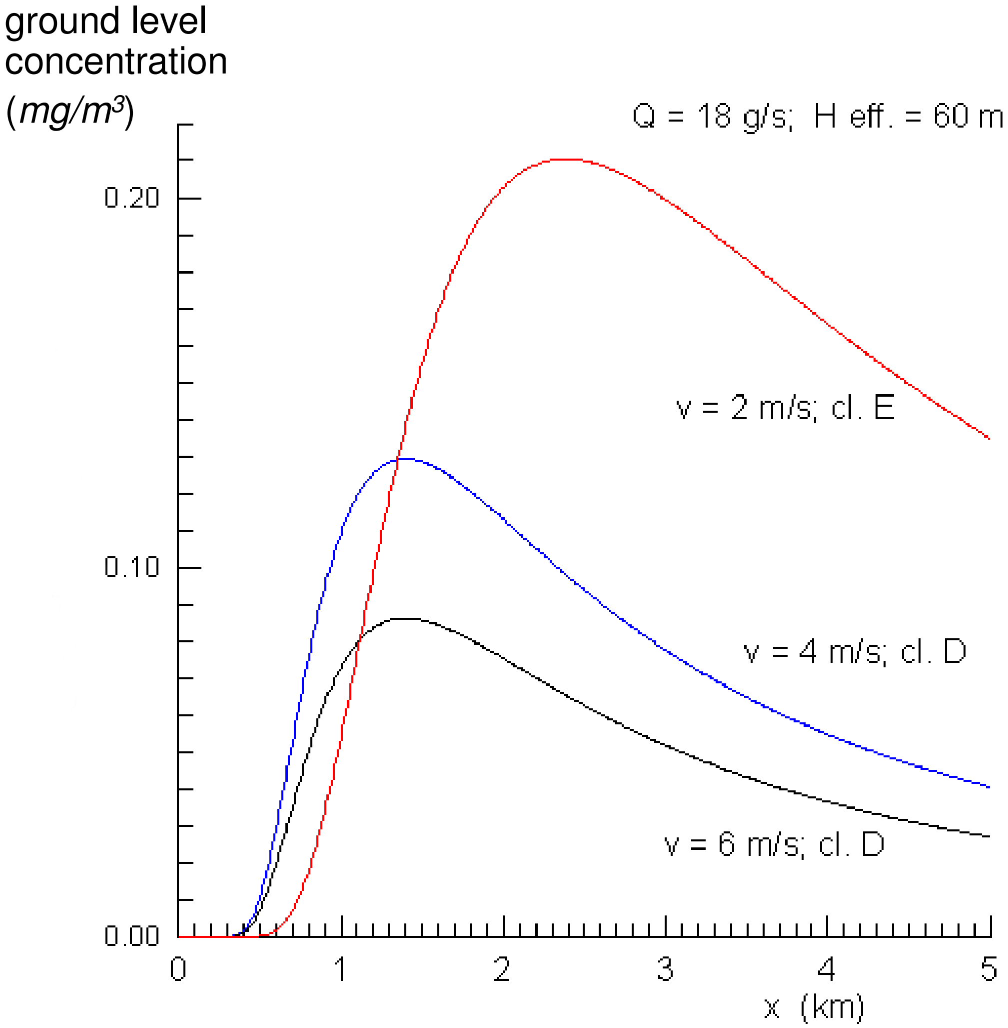
C_{max}= 1.0 10^{-4} g/m^3; x_{max} = 1.4 *km*



Q = 18 *g/s*; u = 5 *m/s*; H = **90** *m*; Stab. class = D

C_{max}= 0.43 10^{-4} g/m^3; x_{max} = 2.4 *km*

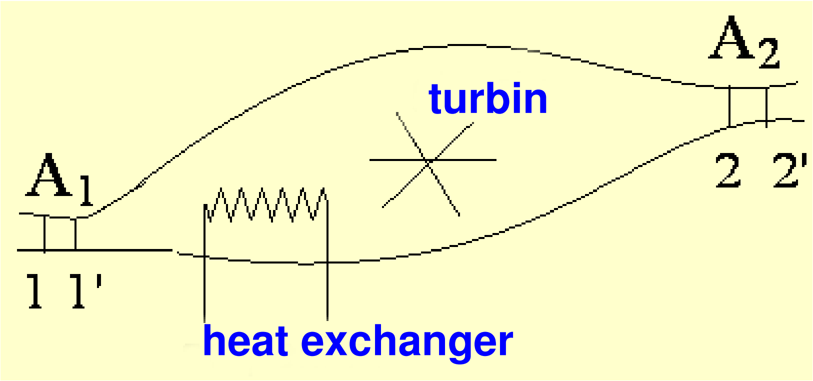
EFFECT OF WIND SPEED



A large wind speed favors dispersion (this term appears at the denominator of the pre-exponential term). In the case of nocturnal emission, in addition, the stability class from sub-adiabatic becomes adiabatic with increasing wind speed (see slide 34). Also under sunny conditions, although super-adiabaticity is reduced, the overall effect of the wind speed favors dispersion.

INTEGRAL ENERGETIC BALANCE

Bernoulli's equation



The control volume can exchange mechanical and thermal energy (through a turbin and a heat exchanger, respectively) with its surroundings. In sections 1 and 2 the speed is perpendicular to surface *A*.

Ac = En – Ex (+ Cr = 0)

$dE_{TOT} = E_{TOT}(t+dt) - E_{TOT}(t)$

As for the total mass in a chemical reaction, the term Cr is null. However, various forms of energy must be taken into account. The volume is that between 1-2 at time *t*, and 1'-2' at time $t + dt$.

The total energy per unit mass is : $\boldsymbol{E = U + \frac{1}{2} v^2} + g \, . \, z$ (where: U = internal energy; v = velocity of the center of mass; $g \, . \, z$ = gravitational energy). (En – Ex) accounts for the mechanical and thermal energy exchanged between the control volume *V* and its surroundings :

$dE_{TOT} = Q\,dt - W\,dt$ (1st law of thermodynamics), where Q and W are heat and work exchanged per unit time.

In addition to the mechanical work (W_u), the volume work exchanged between the system and surroundings must be taken into account:

$dW = F.dl = P.dV = P\,A <v> dt$

Multiplying by $V\rho = 1$ (in fact, V per unit mass is the reciprocal of density) and recalling that

$\omega = \rho\,\Psi = \rho <v> A$

$\Rightarrow \qquad dW = P\,V\,\rho\,A <v> dt \;= P.V.\omega\,dt$

$\Rightarrow$ W (per unit time) = $W_u + \Delta_{2,1}(P.\,V.\,\omega)$

Therefore, ΔE_{TOT} (all terms per unit time) =

$= \int_1^2 [\partial\,(E.\rho)/\partial t]\,dV + \Delta_{2,1}[(U + \frac{1}{2}\,v^2 + g\,.\,z)\,.\,\omega] =$
$= Q - W_u - \Delta_{2,1}(P.\,V.\,\omega)$

where the first term accounts for possible mass variations with time within the control volume (E = energy/mass), and is = 0 if no mass changes occur , that is, $dm/dt = \omega^{En} - \omega^{Ex} = 0$.

Under stationary conditions (**ω = const**.), dividing by ω the **Bernoulli equation** is obtained :

$\Delta_{2,1}(U + \frac{1}{2}\,v^2 + g.z) = q - w_u - \Delta_{2,1}(P\,V\,)$

$\boldsymbol{\Delta_{2,1}(U + \frac{1}{2}\,v^2 + g\,.\,z) + \Delta_{2,1}(P\,V\,) = q - w_u}$

where $q = Q/\omega$ e $w_u = W_u/\omega$ represent, respectively, the thermal and mechanical energy per unit mass, and V is the volume per unit mass.

Other forms of the Bernoulli equation: with all quantities referred to unit mass, and $H = U + PV$,

$\Delta_{2,1}(U + ½\,\mathrm{v}^2 + \mathrm{g}\,.\,z) + \Delta_{2,1}(P\,V) = \mathrm{q} - \mathrm{w_u}$

can be formulated as → $\boldsymbol{\Delta_{2,1}(H + ½\,\mathrm{v}^2 + g\,z) = \mathrm{q} - \mathrm{w_u}}$

or, recalling that $d\,U = d\,\mathrm{q} - P\,d\,V$ in the absence of frictional energy dispersion of the fluid (only expansion work) → $\boldsymbol{\Delta_{2,1}(½\,\mathrm{v}^2 + g\,z) + \int_1^2 V\,d\,P = -\,\mathrm{w_u}}$

A frequently met situation occurs when a **fluid flows in a pipe with no mechanical work** **($\mathrm{w_u} = 0$) :**

→ $\boldsymbol{\Delta_{2,1}(½\,\mathrm{v}^2 + g\,.\,z) + \int_1^2 V\,d\,P = 0}$

Fluids flowing in a pipe with $\mathbf{w_u = 0}$ **:**

$$\Delta_{2,1}\left(\tfrac{1}{2} v^2 + g \cdot z\right) + \int_1^2 V\, dP = 0$$

INCOMPRESSIBLE FLUIDS

$V = 1/\rho$, $\Delta v = 0$; the **static equation** for incompressible fluids (**ρ = constant**) is obtained:

$\rightarrow \quad \Delta_{2,1}(g \cdot z + P/\rho) = 0 \qquad (\rho = \text{const.})$

in differential terms : $\mathbf{g}\, dz + dP/\rho = 0$

APPLICATIONS

It can be easily verified that for a **water** mass at rest a pressure difference of **1 *atm*** (101325 *Pa*) corresponds to a depth of **10.33 *m***.

$\Delta_{2,1}(\tfrac{1}{2} v^2 + g\, z + P/\rho) = 0 \qquad$ where $\Delta v = 0$

$dP/dz = -\rho\, g \qquad$ that is : $\quad \Delta z = -\Delta P/(\rho\, g)$

$\Delta z_{(m)} = -\, 101325\ Pa\, /\, (10^3\ kg/m^3 \times 9.807\ m/s^2) = -\, 10.33\ m$

GASEOUS FLUIDS ⇒ variable ρ

$\rightarrow\ dP/dz = -\rho \cdot g \qquad$ as seen above

N.B. *P* decreases with increasing *z*.

This relationship is the same as that shown above for incompressible fluids, but here the density **ρ can change with *z***. Reminding that $P V = n R T$:

$\rho = M n / V = M P / R T \qquad$ (where M = molecular mass)

$\rightarrow\ dP/dz = -\, M P g / RT$

$d \ln P = -\, (M / RT)\, g\, dz$

RAREFACTION OF THE ATMOSPHERE WITH ALTITUDE

assuming T is const.: $dP/P = d\ln P = -(M^{air}/\mathrm{R}T)\,g\,dz$

$$\Rightarrow \quad \ln(P_2/P_1) = -(M^{air}/\mathrm{R}\,T)\,.\,g\,(z_2 - z_1)$$

N.B. M^{air} = weighted mean of the molecular masses of nitrogen (80%) and oxygen (20%).

$M^{air} = \Sigma_k \mathrm{Y}_k . M_k = 28 \times 0.8 + 32 \times 0.2 \approx 29\ g/mol$

$\approx 0.029\ kg/mol$

N.B. $\rho^{air} = M^{air} . P/(\mathrm{R}\,T) = 0.029\ kg/mol\ .\ 101325\ Pa/(8.314\ J/K^{-1}\ mol^{-1} . 273\ K) = 1.29\ kg/m^3$ (at $P = 1\ atm$ and $T = 0\ °C$), that is, 775 times smaller than that of water.

REDUCTION OF ATMOSPHERIC PRESSURE WITH INCREASING ALTITUDE

$\ln(P_2/P_1) = -(M^{air}/\mathrm{R}\,T)\,.\,g\,(z_2 - z_1)$

At 2000 m above sea level, with $T = 273\ K$:

$\ln(P_{(atm)}/1\ atm) = -0{,}029\ kg\,mol^{-1} .\ 9.81\ ms^{-2} .\ 2000\ m/(8.314\ JK^{-1}\ mol^{-1} . 273\ K) \Rightarrow \ln P = -0.25$

$\Rightarrow P = 0.778\ atm$

At $z = 5000\ m \rightarrow P = 0.535\ atm$

N.B.: the greatest approximation is the assumption that T is constant in the equation relating P to z.

TEMPERATURE DECREASE WITH ALTITUDE

Equation $\Delta_{2,1}(H + \frac{1}{2} v^2 + g\,z) = \mathrm{q} - \mathrm{w_u}$ allows one to evaluate easily the **temperature decrease with increasing altitude** under **adiabatic conditions** ($\mathrm{q}=0$). Assuming a vertical velocity = 0, given that $\mathrm{w_u} = 0$, the equation simplifies to

$\Delta_{2,1}(H + g\,z) = 0$ or, in differential form, $(dH_\mathrm{P} = \mathrm{C_P}\,dT)$

$\mathrm{C_p}\,dT + g\,dz = 0 \quad \Rightarrow \quad (dT/dz)_{\mathrm{adiab.,\,dry}} = -\,g\,/\,\mathrm{C_p}$

N.B. The water vapor contained in humid air condenses to liquid H_2O when the temperature decreases, thus producing heat and reducing air cooling.

For a diatomic ideal gas (air) at room T there are 5 degrees of freedom (a total of 6, but the vibrational one is not active)

$\Rightarrow \quad U = 5/2\ \mathrm{nR}T\ ; \quad H = 7/2\ \mathrm{nR}T$

All energy terms are referred to unit mass:

$\mathrm{C_p}/mole = 7/2\ \mathrm{R}\ ;\ \mathrm{C_p}/kg = 7/2\ \mathrm{R}\,/\,\mathrm{M}^{air}$ ($\mathrm{M}^{air} \approx 0.029$ kg/mol) ; $\mathrm{C_p} = 7/2 \times 8.314/0.029 \approx 1000\ J\,K^{-1}\,kg^{-1}$

$\rightarrow \quad (dT/dz)_{\mathrm{adiab.,\,dry}} \approx -\,0.01\ K/m$

Air cooling is about **1 degree per 100 *m* altitude**.

WARM WIND *(Föhn)* – When a body of air passes overmountains it cools, inducing condensation of its water vapor (clouds and rain/snow on mountain tops). During the opposite process of moving downhill to the valley, the body of air warms up: this is the so-called ***Föhn***, a well known phenomenon in the Alps. Assuming a vertical velocity = 0, the temperature increase is described by the same equation.

TRANSPORT OF THERMAL ENERGY

Heat (Q) transfer between system and surroundings can take place through various mechanisms:

1. **CONDUCTION** – Heat flow is due to a temperature gradient. (Internal) energy is exchanged through molecular collisions (occupation of higher translational, rotational and vibrational levels).

Fourier's law, analogous to Fick's 1st law, applies :

Flux of **Q** along the *x* axis: $\mathbf{q_{s,t} = -K_T \cdot (\partial T/\partial x)}$

where $q_{s,t}$ = heat per unit time and surface

and K_T = thermal conductivity.

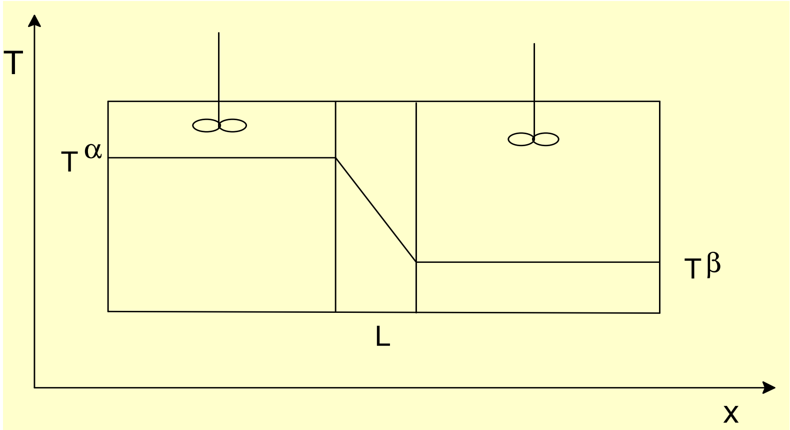
The flux through a plate of thickness L in contact with thermal tanks at $T = T^\alpha$ e T^β , under steady state conditions:

$$q_{s,t} = K_T \cdot \Delta_{\alpha,\beta} T / L$$

2. **CONVECTION** – When the two values of T in phases α and β are kept constant by stirring while heat flows along *x*:

$$\mathbf{q_{s,t} = K'_T \cdot \Delta_{\alpha,\beta} T / L}$$

the same as in conduction, but with a larger K'_T (in analogy with turbulent diffusion).



N.B.: the units (S.I.) of K_T are:

$J\,s^{-1}\,m^{-1}\,K^{-1}$

$\equiv W\,m^{-1}\,K^{-1}$

EXERCISE

HEAT FLUX THROUGH A WALL.

A wall has a thickness of 5 *cm*, and internal and external temperatures of 20 °C and 5°C, respectively.

Evaluate the heat flux ($q_{s,t}$) for two materials with different thermal conductivities: bricks ($K_T = 0.69\ W\ m^{-1}\ K^{-1}$) or wood ($K_T = 0.208\ W\ m^{-1}\ K^{-1}$).

Assume that: 1) thermal conductivity variations with temperature are negligible; 2) heat transfer occurs along a single direction (through the wall thickness).

Bricks **:**

$q_{s,t} = K_T \,.\, \Delta_{\alpha,\beta} T / L = 0.69\ W\ m^{-1}\ K^{-1} \,.\, (20 - 5)\ K / 0.05\ m$

$= 207\ W\ m^{-2}$.

Wood ***:***

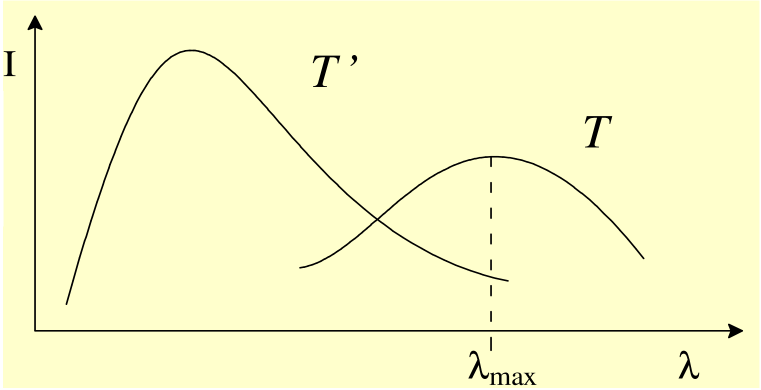
$q_{s,t} = 0.208\ W\ m^{-1}\ K^{-1} \,.\, (20 - 5)\ K / 0.05\ m = 62.4\ W\ m^{-2}$.

Because of their larger thermal conductivity, the heat loss through bricks is faster.

TRANSPORT OF THERMAL ENERGY

3. **THERMAL RADIATION** – The surface of a (black) body in thermal equilibrium emits energy in the form of electromagnetic radiation. The spectrum of emitted wavelengths (λ) depends on the body temperature:

I = flux of electromagnetic energy.



The total energy emitted is proportional to T^4 :

$$\mathbf{I_{tot} = \int_0^\infty I \, d\lambda = C_{SB}} \, T^4$$ (***Stefan-Boltzmann*** equation)

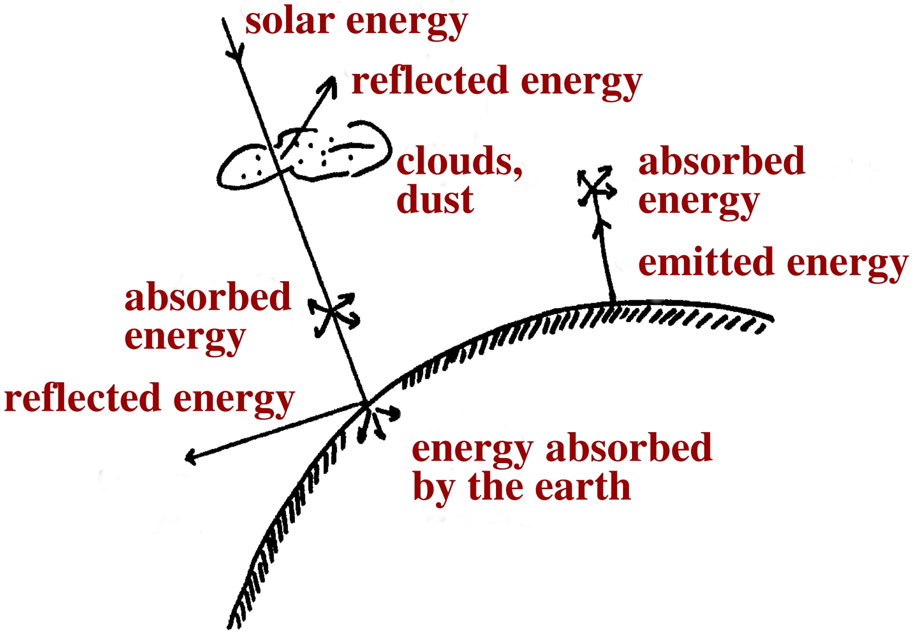
When T decreases λ of the emitted radiation is shifted towards higher values (smaller energy) according to :

$$T \cdot \lambda_{max} = \mathbf{const.}$$ (***Wien*** equation)

(note that $Energy = h\nu$ and $\nu = c/\lambda$, with h = *Planck* constant = 6.6×10^{-34} $J\,s$, c = speed of light)

The solar radiation (emitted at very high temperature) includes plenty of ultraviolet radiation, while the radiation emitted by the surface of the earth is mainly infrared. For this reason, the greenhouse effect is determined by gases which absorb infrared radiations (leading to excitation of vibrational levels).

GREENHOUSE EFFECT



It is an atmospheric-climatic phenomenon of a planet which increases its retention in its atmosphere of a part of energy from the solar radiation. It plays an important role in the complex mechanisms which determine the thermal equilibrium of a planet and acts by means of gases present in the atmosphere, referred to as greenhouse gases.

It is worth noting that <u>in the absence of this effect the average temperature</u> of the planet would be about 30 degrees lower, that is, it <u>would fluctuate around -18 ° C</u>, well below the freezing temperature of water, with obviously catastrophic effects for life on Earth.

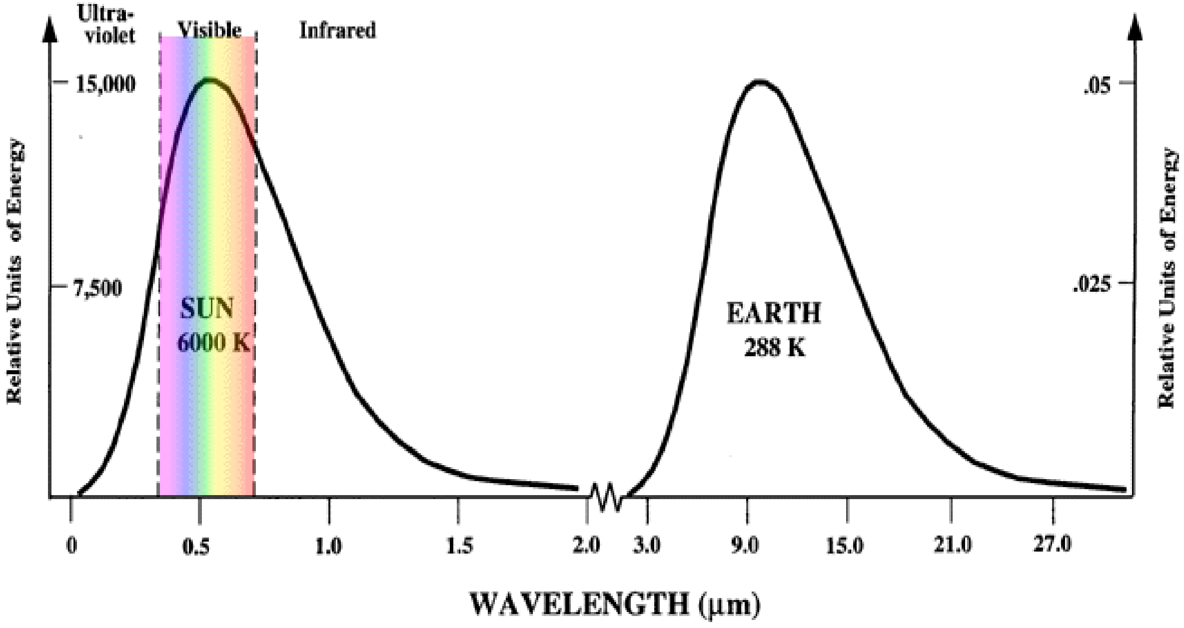
The constant temperature increase observed over the past decades might be due to continuous introduction into the troposphere of greenhouse gases (mainly CO_2), associated with anthropogenic activities (transport, heating, industry, …).

From a different point of view, the main cause is to be traced back to a reduced volcanic activity over the past few centuries, recalling that the atmospheric dust reflects solar radiations, thus acting in the opposite direction.

Even regarding the extent of harmful effects there is some disagreement. Anyway, greenhouse gases contribute to increase the atmospheric temperature, so that their introduction into the atmosphere must be limited.

The Earth's surface emits infrared (IR) radiations with a peak at $\lambda_{\max} \sim 10\ \mu m$, ~ 10^{-3} *cm*, that is, $\nu \sim 1000\ cm^{-1}$). During the night the air cools, this effect being attenuated by a cloudy overcast sky, which reduces the dispersion of radiations. This mechanism can be altered by the presence of gases which absorb IR radiations, thus capturing energy. Then thermalization of the absorbed radiant energy takes place through molecular collisions, thus leading to a temperature increase of the atmosphere.

Contributions to the greenhouse effect come from various gases present in the atmosphere: water vapor (67%), carbon dioxide (15%), methane (8%). Water vapor does not have anthropogenic origins, but temperature increases do lead to an increase in the water vapor present in the atmosphere.



Emission spectra of Sun and Earth.

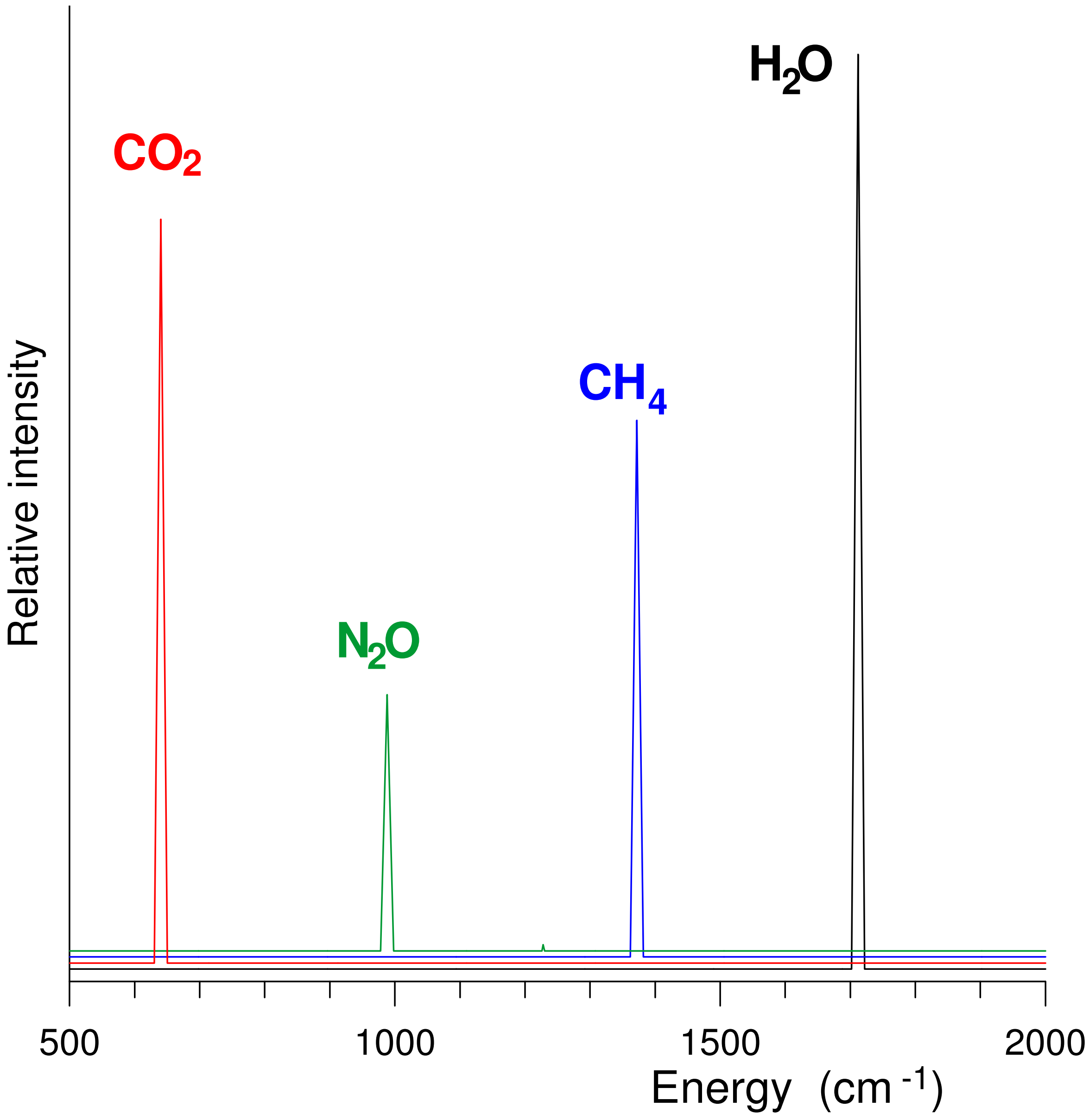
Note that the product $T \times \lambda_{max}$ is nearly equal for the Sun (6000 *K* x 0.5 µm) and the Earth (300 *K* x 10 µm) surface. Also note the very large difference in the amount of energy emitted by the Sun (left-hand scale) and Earth (right-hand scale), the former being more than 5 orders of magnitude larger.

Greenhouse gases reduce the dispersion of infrared radiations. Solar radiations tend to “bounce” from the soil towards the atmosphere. Greenhouse gases prevent their complete dispersion in the outer space, acting like a huge greenhouse. The problem arises because too large amounts of greenhouse gases are introduced in the atmosphere, mainly carbon dioxide due to combustion of coal and oil.

The concentration being the same, the effect produced by CH_4 is 23 times larger than that of CO_2, the effect of N_2O being even much larger (310 times), due to their different capacities to absorb at the wavelengths of IR radiations emitted by the soil.

Arrhenius (the same scientist who found the dependence of the kinetic constant on temperature), in 1896 on the basis of the first IR rays observations of the Moon by Langley, for the first time predicted a temperature increase of the Earth as a consequence of an increase of CO_2 in the atmosphere.

The temperature increase of the Earth will produce more and more extreme meteorological phenomena, such as hurricanes, storms and floodings, will cause a continuous melting of polar glaciars, raising of the sea level and disappearence of most of the present coastlines.



Gas-phase IR spectra as calculated at the B3LYP/6-31G(d) level of theory.

APPENDIX

CHEMICAL KINETICS - Reaction rates

To evaluate the reaction term $\nu_k r = \nu_k \, dC_k/dt$ (where the stoichiometric coeff. ν_k has a positive sign for products and a negative sign for reagents) and its effects over time, one needs a mathematical expression form for concentration changes as a function of time, namely, the ***kinetic equation***.

For a generic net reaction

$$\nu_a \mathrm{A} + \nu_b \mathrm{B} + \ldots \rightarrow \nu_c \mathrm{C} + \nu_d \mathrm{D} + \ldots$$

the reaction rate (v) can be expressed as :

$$\mathrm{v} = -\,dC_A/dt \quad \text{or} \quad -\,dC_B/dt \quad \text{or} \quad dC_C/dt \quad \text{or} \; dC_{\mathrm{D}}/dt \;\ldots$$

- The derivative is preceded by a negative sign "–" for the reagents (their change with time is negative), so that v will be positive;

- v is a function of the concentration (intensive property) of some species, not of mole number (which depends on the system dimensions);

- given that concentrations change continuously during a reaction, the velocity v also changes with time.

- depending on the species to which v refers, its value changes in proportion to the stoichiometric coefficient of that species in the reaction. The symbol *r* refers to a coefficient = 1.

Kinetic equations of **monomial form** (product of a constant K and powers of concentrations) such as, for instance,

$$-dC_A/dt = K \, . \, C_A{}^{na} \, . \, C_B{}^{nb} \, . \, C_C{}^{nc} \ldots$$

are frequently encountered and their solutions are relatively less complex.

1) The exponents n_a, n_b, n_c, ... DO NOT generally coincide with their corresponding stoichiom. coefficients ν.
2) The kinetic law, monomial or more complex, CAN NOT be deduced a priori from the stoichiometry.
3) Generally, but NOT always, the concentrations of products are not involved in the kinetic equation.

REACTION MECHANISM

Points 1-3 listed above are a consequence of the fact that the net reaction described by the stoichiometry generally <u>does not occur with a single reactive event</u> (**elementary step**) where the reagents directly generate the products, but through a <u>sequence of elementary steps</u>. For example, the three-step mechanism :

$$\begin{array}{l} A + B \rightarrow 2\,C \\ 2\,C \rightarrow D \\ D \rightarrow E + F \\ \text{--------------------} \\ A + B \rightarrow E + F \end{array}$$

leads to this net reaction because species C and D (reaction intermediates) are first generated and then consumed. The net reaction represents the sum of the various elementary steps.

If the rates of the three steps are comparable, then the velocity of formation of the products is a combination of the three single rates; if one of the steps is much slower than the others, its velocity will limit the velocity of the whole reaction; in contrast, the rate of a step much faster than the others will not influence the reaction rate.

As a consequence, the kinetic equation can not be predicted a priori on the basis of the stoichiometry, but it must be experimentally determined.

Only for an elementary step can the kinetic equation be deduced from the stoichiometry. Both the two main kinetic theories, the ***collision theory*** and the ***theory of the activated complex*** (not considered here), demonstrate that

→ for an ***elementary step*** the reaction rate is the product of a constant (to be determined experimentally) and the concentrations of the reagents, each raised to a power equal to the stoichiometric coefficient.

For instance, for the elementary steps:

A → products $v = K\, C_A$
A + B → products $v = K\, C_A\, C_B$
2 A → products $v = K\, C_A^2$
A + 2 B → products $v = K\, C_A\, C_B^2$

etc. ...

N.B.: the contrary is not true, i.e., these kinetic equations are not necessarily associated with an elementary step.

Only for kinetic equations of monomial form (see slide N. 20) can a **reaction order** (n) be defined: $n = n_a + n_b + n_c + \ldots$, where n_a , n_b , n_c are the powers of concentrations and are called partial orders relative to the single species.

TEMPERATURE effect **: Arrhenius' law**

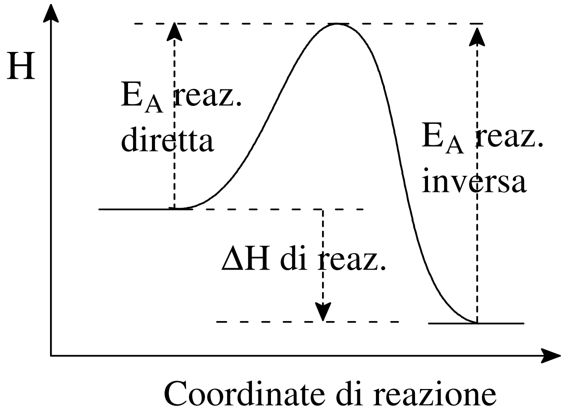
Arrhenius (1889), who knew *van't Hoff's* equation (dependence of K_{eq} on T) and experimental evidence for a strong dependence of the kinetic constants from temperature, predicted and verified experimentally the **exponential dependence** of the kinetic constant K upon Temperature :

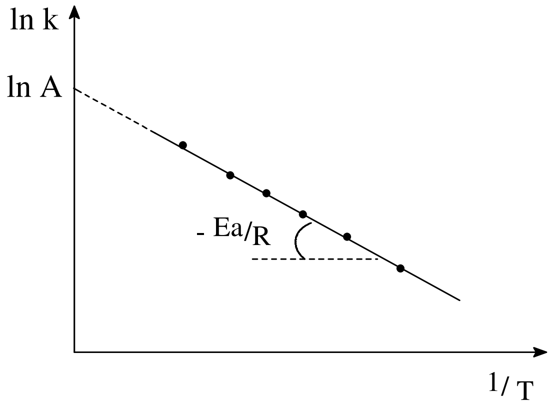
$$\frac{d \ln K}{d T} = \frac{E_A}{RT^2} \qquad \text{(in differential form)}$$

$$\Rightarrow \quad \ln K = -\frac{E_A}{RT} + \ln A \quad \Rightarrow \quad \boxed{K = A.e^{-\frac{E_A}{RT}}}$$

where A (***pre-exponential factor***) represents the collision frequency of the reagents *and* E_A (***activation energy***) the energy barrier to be overcome to change reagents into products.

For the products to be formed it is necessary to break one or more bonds of the reagents. Even in the case of the formation of products more stable than the reagents, an energy barrier must first be overcome.





→ $\ln K = -(E_A/\mathrm{R}T) + \ln A$: in order **to determine E_A ed A**, measurements of K values as a function of T must be carried out; then, a plot of ln K vs. $1/T$ gives a linear correlation with slope = $-E_A/\mathrm{R}$ and (extrapolated) intercept = ln A.

$K = \mathrm{A} \cdot \mathrm{e}^{-(E_A/\mathrm{R}T)}$: with an average E_A value of about 50-60 *kJ/mol* at room *T*, a temperature increase of 10 ℃ causes an increase in *K* by a factor 2-3, while halving the E_A (as the action of enzymes can do) leads to an increase in *K* by a factor 10^5 (5 orders of magnitude).

INTEGRATED KINETIC EQUATIONS

In a differential form, kinetic equations correlate the reaction rate to concentrations, while the experimental data typically consist of the determination of the concentration in one species as a function of time.

For a generic reaction : A + *b* B + ... → products

the simplest case occurs when the reaction rate is a function of the concentration of a **single species** :

$$v = -\frac{d\,C_A}{d\,t} = K\;C_A^n$$ (differential kinetic eq.)

where *n* (= 0, 1, 2, 3) is the partial order relative to species A (and also the total order). Separation of variables gives:

$$-d\,C_A/C_A{}^{\mathrm{n}} = K\,dt \qquad \Rightarrow \qquad -C_A{}^{-\mathrm{n}}\;d\,C_A = K\,dt$$

Recalling that $\int x^{\mathrm{n}}\, dx = [1/(\mathrm{n}+1)]\,.\, x^{(\mathrm{n}+1)}$, integration is performed between the initial concentration $C_{A(0)}$ (corresponding to time $t = 0$) and any concentration C_A (corresponding to time t). The following relationship is obtained :

$$\frac{1}{n-1}\left(\frac{1}{C_A^{n-1}} - \frac{1}{C_{A(0)}^{n-1}}\right) = K\,(t-0) = K\,t$$

that is, the integrated kinetic equation for orders ***n* = 0, 2, 3**. In fact, this general equations does not hold for $n = 1$ because a denominator $(\mathrm{n}-1) = 0$ is not acceptable.

For ***n* = 1** :

$$-\int_{C_{A(0)}}^{C_A} \frac{d\,C_A}{C_A} = \int_0^t K\,dt \quad \Rightarrow \quad \ln\frac{C_A}{C_{A(0)}} = -K\,t$$

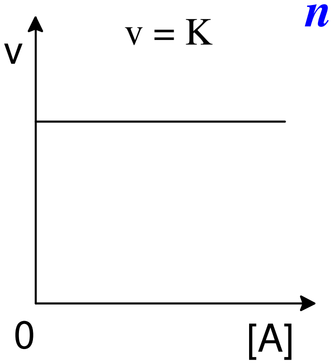
or in exponential form : $C_A = C_{A(0)}\, \mathrm{e}^{-K\,t}$

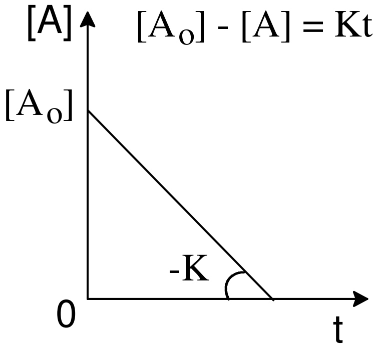
First-order kinetics are frequently encountered. Generally, they are not associated with a (monomolecular) elementary step, but derive from a reaction mechanism. For instance, the rate law of enzymatic catalysis, although more complex, may often be simplified to a first-order equation. The radioactive decay of unstable nuclei (^{14}C is used for dating vegetal or animal materials) follows first-order kinetics. In this case the reaction proceeds through a single monomolecular elementary step, where each single particle has a given probability (over time) to split into 2 or more smaller particles.

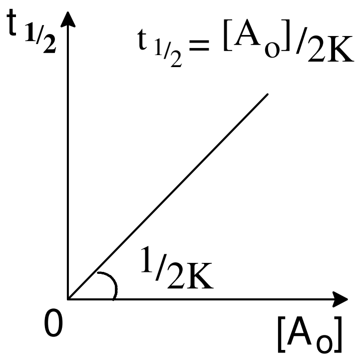
ORDER *n* RELATIVE TO A SINGLE REAGENT

Differential kinetic eq. **Integrated kinetic eq.** **Half time**

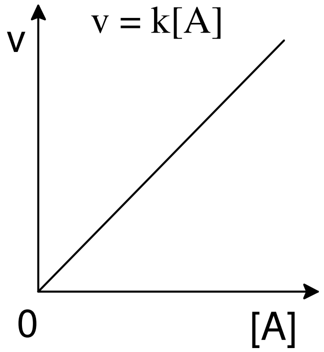
n = 0

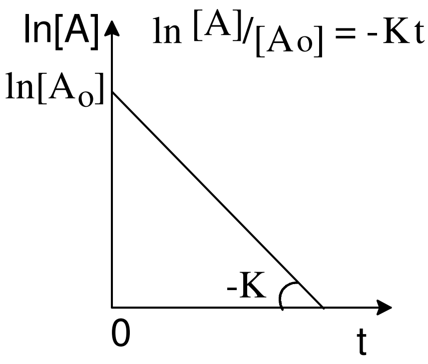


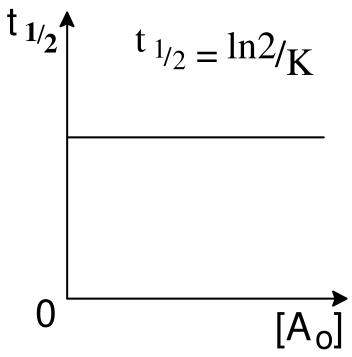




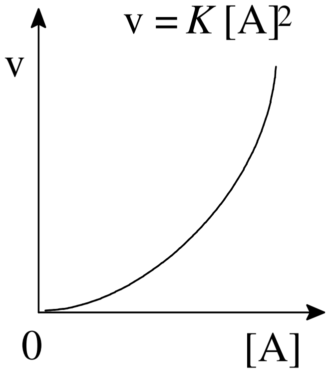
n = 1

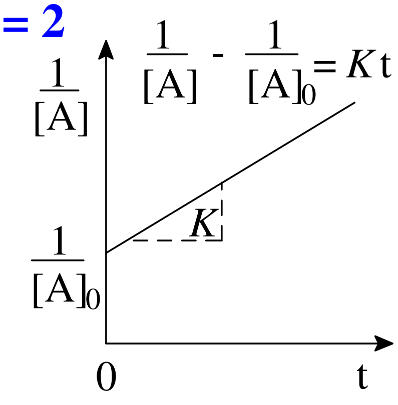


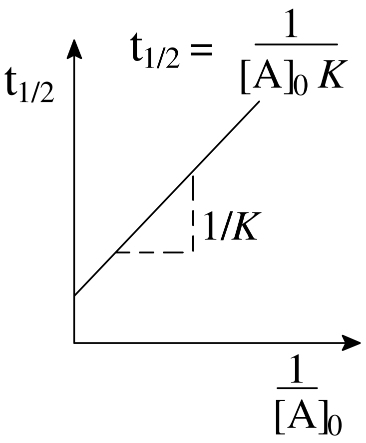




n = 2







HALF-LIFE PERIOD METHOD

From equations $\frac{1}{n-1}\left(\frac{1}{C_A^{n-1}}-\frac{1}{C_{A(0)}^{n-1}}\right)=K\,t$ and $\ln\frac{C_A}{C_{A(0)}}=-K\,t$ (replacing C_A with $C_{A(0)}/2$) the time ($t_{1/2}$) required to halve the initial concentration can be easily obtained:

n	$t_{1/2}$
0	$C_{A(0)}/(2K)$
1	$\ln 2/K$
2	$1/(C_{A(0)}K)$

$t_{1/2}$ increases with the initial concentration for n = 0, is constant for n = 1, and decreases for n = 2. Measurements of $t_{1/2}$ as a function of $C_{A(0)}$ allow one to determine the order and value of the kinetic constant.

EXERCISE – The **^{14}C** radioactive isotope of carbon constitutes about 1 part per trillion of atmospheric carbon, and is formed in the tropo- and stratosphere by interactions between cosmic rays and nitrogen. ^{14}C decays to nitrogen (^{14}N) with an average half-time of 5730 years. The radioisotope is continuously produced thus maintaining its atmospheric equilibrium, and in living organisms the ^{14}C percentage relative to those of the two stable isotopes ^{12}C and ^{13}C remains constant. After the death of the organism, however, the ^{14}C concentration gradually decreases following a first-order kinetic law.

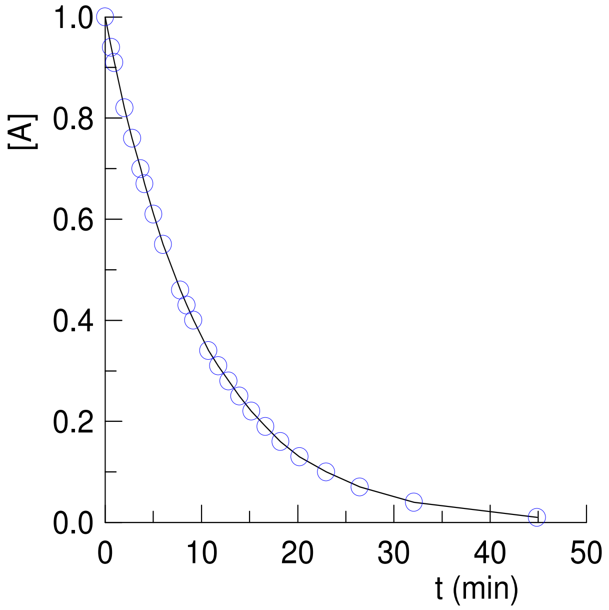
Evaluate the age of a mummy with a 52% ^{14}C content relative to that of living organisms.

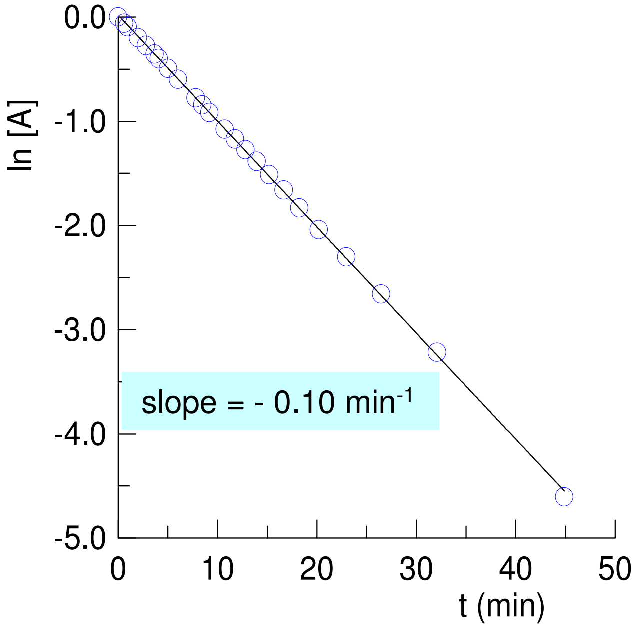
$5730\ years = \ln 2/K \quad\rightarrow\quad K = 1.21 \times 10^{-4}\ years^{-1}$

$52 = 100 \exp(-K\,t) \quad\rightarrow\quad t = -\ln(52/100)/K = 5404\ years$

The most common method to obtain the kinetic equation and the value of the constant *K* is to measure a series of concentration values as a function of time. For instance:

t (min)	[A] (mol/L)	ln [A]
0,0	1,0	0
1,0	0,91	-0,09431
1,3	0,88	-0,12783
2,0	0,82	-0,19845
2,8	0,76	-0,27443
3,7	0,70	-0,35667
4,5	0,64	-0,44628
5,5	0,58	-0,54472
6,0	0,55	-0,59783
7,2	0,49	-0,71335
8,5	0,43	-0,84397
9,2	0,4	-0,91629
10,7	0,34	-1,07881
11,7	0,31	-1,17118
12,8	0,28	-1,27296
15,2	0,22	-1,51412
16,7	0,19	-1,66073
18,2	0,16	-1,83258
20,2	0,13	-2,04022
22,9	0,10	-2,30258
26,5	0,07	-2,65926
32,1	0,04	-3,21887
44,8	0,01	-4,60517





With these data, the diagram concentration-time (not linear) rules out a zero-order law. A diagram ln [A] vs. t displays a good linear correlation, thus indicating a first-order kinetic law. The slope supplies the value (0.10 *min*$^{-1}$) of the kinetic constant *K*. $t_{1/2} = \ln 2/K$ turns out to be 6.9 *min*, as approximately verified from the diagram *conc.- t*.

ISOLATION METHOD

The integrated equations considered above hold only when $v = -d[A]/dt = K [A]^n$,i.e., if the velocity depends on the concentration of a single species. Often, in contrast, the velocity depends on the concentrations of two or more species, and the integrated kinetic equations become more complex. However, it is possible to operate under laboratory conditions which allow the use of the same kinetic equations derived above.

Suppose that for the reaction $A + B \rightarrow$ *products* the kinetic equation is $-d[A]/dt = K [A]^{na} [B]^{nb}$.

If the initial concentration of species B is in large excess relative to that of A (for instance, $[B]_0 = 100\,[A]_0$), once A has been completely consumed, only 1/100 of B has reacted. Therefore, the concentration of B (and its contribution to the reaction rate) remains almost constant,

$\Rightarrow \quad -d[A]/dt = K_{obs} [A]^{na}$, where $K_{oss} = K [B]_0^{nb}$.

Once *n*a has been determined, in other kinetic runs species B can be isolated (with a large excess of $[A]_0$), and *n*b can be determined. From the values of K_{obs}, $[B]_0$ and $[A]_0$ the kinetic constant *K* can then be found.

RELATIONSHIP BETWEEN EQUILIBRIUM AND KINETIC CONSTANTS

Consider the kinetic equations for the two reversibile elementary steps :

$$A + B \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} C \qquad (1)$$

$$C \underset{K_{-2}}{\overset{K_2}{\rightleftharpoons}} D \qquad (2)$$

$$A + B \rightleftharpoons D$$

$$d[\mathrm{C}]/dt = K_1\,[\mathrm{A}]\,[\mathrm{B}] - K_{-1}\,[\mathrm{C}] \qquad (1)$$

$$d[\mathrm{D}]/dt = K_2\,[\mathrm{C}] - K_{-2}\,[\mathrm{D}] \qquad (2)$$

Once the equilibrium conditions are reached, concentrations remain constant, so that

$$K_1\,[\mathrm{A}]\,[\mathrm{B}] - K_{-1}\,[\mathrm{C}] = 0 \qquad (1)$$

$$K_2\,[\mathrm{C}] - K_{-2}\,[\mathrm{D}] = 0 \qquad (2)$$

which can be rearranged as

$$\frac{[C]}{[A]\,[B]} = \frac{K_1}{K_{-1}} = K_{eq1} \qquad (1)$$

$$\frac{[D]}{[C]} = \frac{K_2}{K_{-2}} = K_{eq2} \qquad (2)$$

⇒ The equilibrium constant of each elementary step is the ratio between its direct and inverse kinetic constant.

⇒ The equilibrium constant of the net reaction is the ratio of the product of the direct kinetic constants over the product of the inverse constants:

$$K_{eq} = \frac{[D]}{[A][B]} = K_{eq1} \cdot K_{eq2} = \frac{K_1\, K_2}{K_{-1}\, K_{-2}} = \frac{\Pi\, K_i}{\Pi\, K_{-i}}$$

Therefore, a relationship exists between the equilibrium and kinetic constants. The knowledge of the direct and inverse kinetic constants contains more information than a knowledge of the equilibrium constants. From the kinetic constants the equilibrium constants can be derived, but not viceversa. The equilibrium constant does not reveal whether the direct and inverse kinetic constants are both relatively large or small , that is, whether under non-equilibrium conditions the system will evolve slowly or rapidly toward equilibrium.

DIMENSIONS OF KINETIC CONSTANTS

It is to be noted that, while the dimensions of the reaction rate are always *concentration time*$^{-1}$, the dimensions of the kinetic constant depend on the reaction order:

$$\mathrm{v} = K\,(conc.)^n \equiv conc.\ t^{-1} \;\Rightarrow\; \boldsymbol{K \equiv (conc.)^{-(n-1)}\, t^{-1}}$$

N.B. The numerical value of K thus depends on the choice of concentration (except for $n = 1$) and time units.

ENZYMATIC CATALYSIS

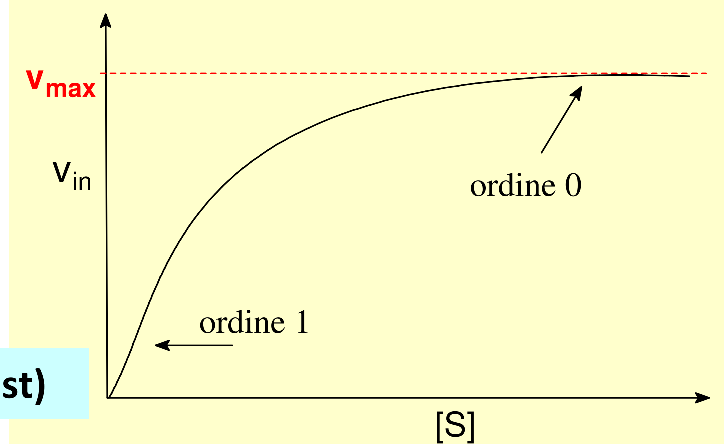
MECHANISM

$$E + S \underset{k_{-1}}{\overset{k_1}{\longleftrightarrow}} ES$$

$$ES \underset{k_{-2}}{\overset{k_2}{\longleftrightarrow}} EP$$

$$EP \underset{k_{-3}}{\overset{k_3}{\longleftrightarrow}} P + E$$

(fast)



According to the **Michaelis-Menten** mechanism, 1) the rate of formation of the product coincides with that of the complex EP (3rd step fast) ⇒ $\mathbf{v = k_2\,[ES]}$

2) Steady state for the intermediate **ES** ⇒ $d[ES]/dt = 0$

$$k_1\,[E]\,[S] - k_{-1}\,[ES] - k_2\,[ES] + k_{-2}\,\cancel{[EP]} = 0\;;$$

$$[E] = [Eo] - [ES] - \cancel{[EP]}$$

When the reaction starts, [EP] e [P] ≈ 0 ⇒ the inverse reactions of the 2nd and 3rd steps can be neglected ⇒ the results strictly hold only for the **initial rates** (v_{in}).

$$[ES] = \frac{k_1\,[E_0]\,[S]}{k_{-1} + k_2 + k_1\,[S]} \quad \Rightarrow \quad \boxed{v_{in} = \frac{k_2\,[E_o]\,[S]}{\frac{k_{-1} + k_2}{k_1} + [S]} = \frac{v_{max}\,[S]}{k_M + [S]}}$$

Limit cases:

$[S] \ll K_M \;\Rightarrow\; v_{in} = K_{obs}\,[S]$ (**order 1**)

$[S] \gg K_M \;\Rightarrow\; v_{in} = v_{max}$ (**order 0**)

$$v_{in} = \frac{k_2\,[E_o]\,[S]}{\frac{k_{-1} + k_2}{k_1} + [S]} = \frac{v_{max}\,[S]}{k_M + [S]}$$

N.B.

- $k_2\,[E_o] = V_{max}$
- In correspondence of $v = V_{max}/2 \rightarrow [S] = k_M$

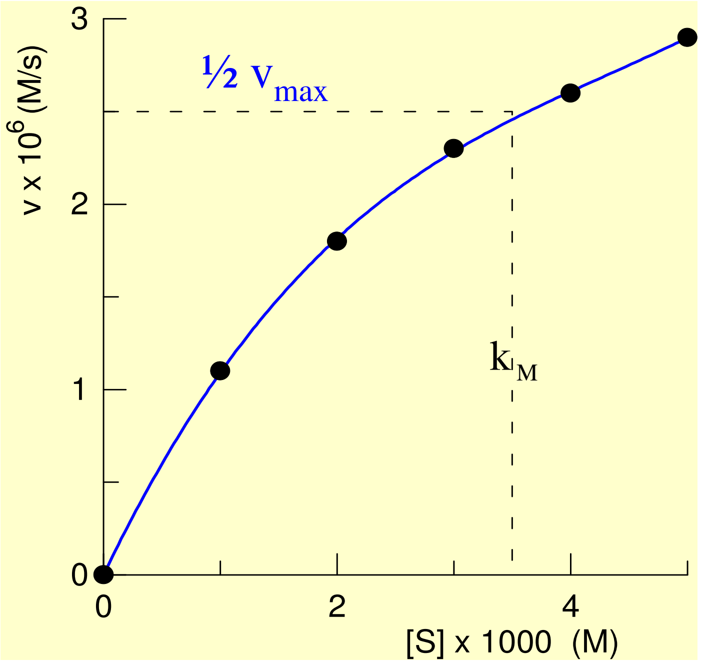
Leonor Michaelis e Maud Menten (University of Berlin). In 1913 they proposed a two-step mechanism for enzymatic catalysis, later refined by Briggs and Aldane.

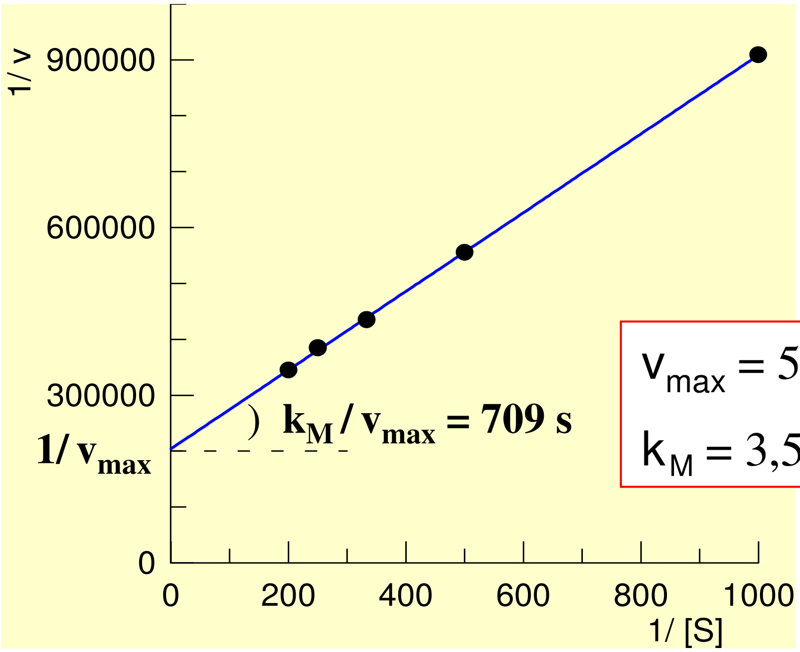
Fixed [Eo], **v_{max}** and **k_M** (Michaelis constant) are the two relevant parameters. Often the available experimental data do not allow a direct determination of v_{max}. The "double-reciprocal plot“ method can be used:

$$\frac{1}{v} = \frac{1}{v_{max}} + \frac{k_M}{v_{max}} \cdot \frac{1}{[S]}$$

Expt. data

[S] mM	v_{in} μM s^{-1}
1,0	1,1
2,0	1,8
3,0	2,3
4,0	2,6
5,0	2,9





$v_{max} = 5 \times 10^{-6}$ M s^{-1}

$k_M = 3{,}5 \times 10^{-3}$ M

O_2 solubility in WATER

T (°C)	Conc. saturaz. (mg/L)
2	**13.8**
4	**13.1**
6	**12.5**
8	**11.9**
10	**11.3**
12	**10.8**
14	**10.4**
16	**10.0**
18	**9.5**
20	**9.2**
22	**8.8**
24	**8.5**
26	**8.2**
28	**8.0**
30	**7.6**

From: P.A. Vesilind et al., *Environmental Engineering*, Cap. 4.

Definition of B.O.D.

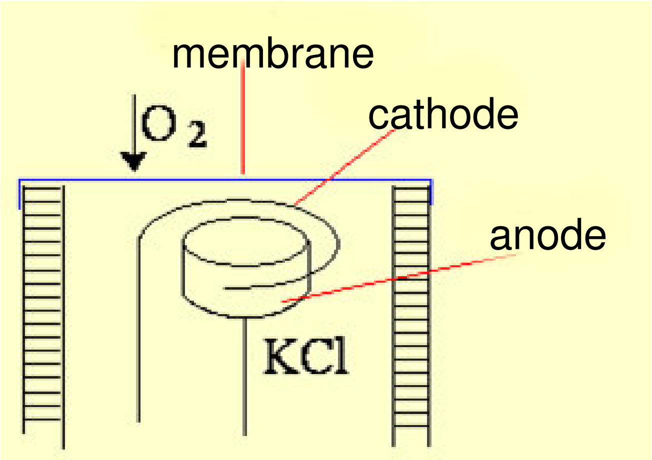
BOD (biochemical oxygen demand) represents the mass of oxygen used in *n* days at 20 °C by microorganisms to decompose organic materials present in 1 liter of water: the notation "BOD_n" (usually BOD_5) means BOD in *n* days.

The maximum concentration of O_2 in water decreases with increasing T. The O_2 concentration can be measured with a polarographic probe, equipped with an Ag anode surrounded by an Au cathode, both immersed in a KCl solution. The bottom teflon membrane is permeable to oxygen. These electrochemical reactions take place:

cathode: $O_2 + 2\,H_2O + 4\,e^- \rightarrow 4\,OH^-$

anode: $4\,Ag + 4\,Cl^- \rightarrow 4\,AgCl + 4\,e^-$

generating a current proportional to the O_2 molecules which reach the cathode.



B.O.D. (Biochemical Oxygen Demand)

Elimination of organic carbon (OR) from waste waters is accomplished by aerobic microorganisms (MO) which, in the presence of O_2, proliferate at the expense of OR, producing CO_2 and other highly oxidated compounds, such as SO_4^{--}, NO_3^{-}, PO_4^{---}, ...

$$\nu_1 O_2 + \nu_2 OR \;\rightarrow\; \nu_3 MO + \nu_4 CO_2 + \dots$$

$$d[O_2]/dt \,.\, 1/\nu_1 = d[OR]/dt \,.\, 1/\nu_2 = d[MO]/dt \,.\, 1/\nu_3$$

(where $\nu_1, \nu_2 < 0\, ;\, \nu_3, \nu_4 > 0$)

The microorganisms increase their mass with time and consume OR following the kinetic law of enzymatic catalysis (Michaelis-Menten mechanism) :

$$d\rho_{MO}/dt = (\mu \,.\, \rho_{MO}) \,.\, \rho_{OR}/(K_M + \rho_{OR})$$

where $\rho_i = C_i M_i$; $\mu \equiv t^{-1}$ (rate per unit MO concentration)

⇒ From the stoichiometry, with $\mathbf{y = |\nu_{3,M}/\nu_{2,M}| > 0}$ (where both the different stoichiometric coefficients and molecular masses are accounted for):

$$-d\rho_{OR}/dt = 1/y \,.\, d\rho_{MO}/dt \;=\; (\mu \,.\, \rho_{MO}/y) \,.\, \rho_{OR}/(K_M + \rho_{OR})$$

with $K_M >> \rho_{OR}$ the equation becomes :

$$-d\rho_{OR}/dt = \mu \,.\, \rho_{MO}/(y\,K_M) \,.\, \rho_{OR} = K_{OR} \cdot \rho_{OR}$$

⇒ first order kinetic ($K_{OR} \equiv t^{-1}$) :

$$\boldsymbol{\rho_{OR} = \rho_{OR}(0) \,.\, e^{-K_{OR}.t}}$$

$-d\rho_{OR}/dt = K_{OR} \cdot \rho_{OR}$

$-d\rho_{O2}/dt = -d\rho_{OR}/dt \, . \, (\nu_{1,M}/\nu_{2,M})$

One can imagine that the whole amount of O_2 required to react completely with OR is already dissolved in water at time $t = 0$ (i.e., $\rho_{O2}(0) = BOD_\infty$) :

$-d\rho_{O2}/dt = (\nu_{1,M}/\nu_{2,M})\, K_{OR} \cdot \rho_{OR} = K_{OR} \cdot \rho_{O2}$

$\Rightarrow \quad \boldsymbol{\rho_{O2}(t) = \rho_{O2}(0)\, e^{-K_{OR}\, t}}$

BOD$_t$ $(mg/L) = \rho_{O2}(0) - \rho_{O2}(t) =$ $\boldsymbol{\rho_{O2}(0) \, . \, (1 - e^{-K_{OR}\, t})}$

According to convention, the oxygen density ρ_{O2} can be indicated by the notation L, so that some texbooks report the equivalent relationships:

$BOD_t = L_0\,(1 - e^{-K_{OR}\, t})$; $L(t) = L_0\, e^{-K_{OR}\, t}$

where $L_0 = \rho_{O2}(0) = BOD_\infty$ = oxygen (*mg/L*) required to oxidize all the initial organic carbon.

→ ρ_{O2} (= L_t) as a function of time can be calculated from the difference $(L_0 - BOD_t) = L_t$ and BOD data, provided L_0 (= BOD_∞) can be determined

→ then, K_{OR} can be found from the slope of the linear plot $\ln \rho_{O2} / t$ (first order kinetic)

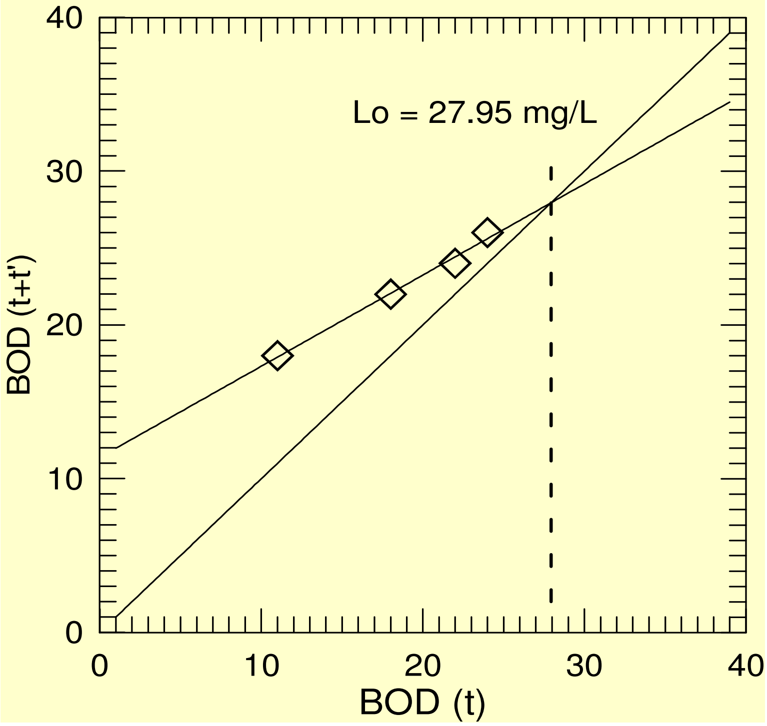
thus obtaining both parameters (**BOD$_\infty$** and $\boldsymbol{K_{OR}}$) which characterize the process. While the former measures the total oxygen demand, the latter is equally important because it describes the kinetics of the process.

Among various methods for elaborating BOD data, one of the most suitable is Fujimoto’s method.

Fujimoto’s method

N.B. – The method requires constant time intervals between subsequent BOD measurements.

t (*days*)	2	4	6	8	10
BOD (*mg/L*)	11	18	22	24	26



The BOD values measured at times *t* (*x* axis) are plotted *vs.* those measured at the corresponding times $t + \Delta t$ (y axis). The L_0 (BOD_∞) value is obtained from the intersection with the bisector

t (days)	L = 27,95 – BOD	ln L
2	16.95	2.830
4	9.95	2.298
6	5.95	1.783
8	3.95	1.374
10	1.95	0.668

From the slope of the linear plot ln L *vs.* t (first-order law) → $K_{OR} = 0.263\ g^{-1}$