# Basic course of tropospheric composition modelling

# Part 2

## Chemical transformations in the troposphere

Current section provides an outline of construction of the chemical transformation mechanism for 3-D Eulerian dispersion models and shows a few simplified examples of the tropospheric chemistry branches.

### Basics of chemical kinetics

Considering the classification of chemical reactions, textbooks usually separate three types of the transformations.

One-body first-order reaction involves only one substance, which is gradually transformed into another one with the speed independent on the actual concentration of either of the agents:

**( 1)** $$[A] \xrightarrow{K} [B]$$

Here *[A], [B]* are concentrations of the agent and the product. In differential form it looks like the following:

**( 2)** $$\frac{d[A]}{dt} = -K_1[A]$$ $$\frac{d[B]}{dt} = K_1[A]$$

Examples of such reactions are: radioactive decay, photolysis, self-degradation of unstable species, etc.

The two-body second-order reaction depends on concentration of both agents:

**( 3)** $$[A][B] \xrightarrow{K_2} [C]$$ $$\frac{d[A]}{dt} = -K_2[A][B]$$ $$\frac{d[B]}{dt} = -K_2[A][B]$$ $$\frac{d[C]}{dt} = K_2[A][B]$$

Majority of the atmospheric reactions can be written in this way.

A three-body third-order reaction still transforms the agents *A* and *B* to agent *C* but it consists of two steps. During the actual conversion an excited atom of *C* is produced, which then needs the presence of the third molecule – usually air, which can take the excess of energy and stabilise the molecule. In absence or lack of the third body the excited molecule falls apart back to the original agents.

( 4)
$$\begin{aligned}
&[A][B] \xrightarrow{M,\,K_3(M)} [C] \\
&\frac{d[A]}{dt} = -K_3(M)[A][B] \\
&\frac{d[B]}{dt} = -K_3(M)[A][B] \\
&\frac{d[C]}{dt} = K_3(M)[A][B]
\end{aligned}$$

An example of such reaction is, for instance, the final stage of the gas-phase oxidation of $SO_2$ to $SO_4^{=}$.

Dependencies of the reaction coefficients on the external conditions can also be of different types and can be described using several theories (leading to different formulas).

### Collision theory

Within the scope of collision theory, the reaction happens when the molecules of the reagents collide with energy sufficient to surpass the energy barrier, called as an activation energy. Probability of the collision is proportional to the agent concentrations, while the probability of the specific molecule to have the energy above the given threshold $E$, in accordance with the Maxwell molecular-kinetics theory, is $exp(-E_{act} /RT)$, where $R$ is the universal gas constant and $T$ is temperature. Therefore, the collision theory for the bimolecular second-order reactions leads to the equation ( 3) with the rate coefficient represented via Arrhenius law:

( 5)
$$K(T) = K_{298} \exp\left(\frac{-E_{act}}{R}\left(\frac{1}{T} - \frac{1}{298}\right)\right)$$

where $K_{298}$ is the rate at temperature 298K.

Collision theory provides good approximations for large fraction of atmospheric reactions but sometimes its too simplistic considerations can lead to large errors in assessing the reaction rates and their dependence on temperature and agent concentrations.

### Transition state theory

Let’s consider the second-order reaction, which results in certain re-arrangements in parts of the agents, essentially leading to creation of the new substances. Let one of the agents be two tightly bounded substances or radicals: B-C. The reaction then results in breakout of this chemical bond and formation of another one with the agent A:

$$A + BC \rightarrow AB + C$$

If both A and BC are molecules, the energy barrier appears far too high and such reactions do not play any role in the atmosphere. However, if one of the agents is a radical, barrier appears substantially lower, so that the reactions between the free radicals and molecules play crucial role in the atmospheric chemistry.

Considerations within the scope of the transition theory assumes that the agents first create an activated complex, also called as transition state, which then breaks out either to the original or new reaction products. The breakout to original products is then in equilibrium with the complex formation reaction:

( 6)
$$A + BC \leftrightarrow ABC^{+} \rightarrow AB + C$$

Its rate depends on both collision probability and the probability of the activated complex to break into the products rather than into original agents:

**( 7)**
$$K(T) = K_{298}^{'} \exp\left(\frac{\Delta S}{R}\right) \ \exp\left(\frac{-E_{act}}{R(T - T_{298})}\right)$$

Here ΔS is the change of the entropy: $\Delta S = S(ABC^{+}) - S(A) - S(BC)$, which characterises the electronic re-arrangements needed for the formation of the activated complex. Should ΔS be independent on temperature, the equation ( 7) turns again into Arrhenius dependence ( 5).

**Pseudo-steady-state approximation. Termolecular reactions.**

Another important type of reactions starts from activation an agent via its collision with the third body (one of molecules of air). Activation is followed by either its second collision with the third body and release of the excess of energy, or a breakout to new products. Similarly, two agents *A* and *B* can form an excited product $AB^{+}$, which stabilization is provided via collision with the third body *M*:

**( 8)**
$$A + B + M \xleftrightarrow{K_{1f},\, k_{1b}} AB^{+} \xrightarrow{K_2} AB + M$$

Corresponding coefficients for initial reaction, release of energy with stabilisation, and the breakout back to initial products are$K_{1f}$, $K_{1b}$, and $K_2$, respectively.

Writing them in a differential form, one obtains:

**( 9)**
$$\frac{d[A]}{dt} = -K_{1f}[A][B] + K_{1b}[AB^{+}]$$
$$\frac{d[AB^{+}]}{dt} = K_{1f}[A][B] - K_{1b}[AB^{+}] - K_2[AB^{+}][M]$$

The pseudo-steady-state theory assumes that the activated intermediary $AB^{+}$ is formed and destroyed so fast that its concentration is essentially always in dynamics equilibrium and thus stationary. This assumption, requires the time derivative in the second equation in ( 9) be zero, which leads to

$$K_{1f}[A][B] = K_{1b}[AB^{+}] + K_2[AB^{+}][M]$$

Then the concentration of the intermediate activated substance $AB^{+}$ will be:

$$[AB^{+}] = \frac{K_{1f}[A][B]}{K_{1b} + K_2[M]}$$

Substituting it into the first equation in ( 9) and noticing that the rate of the generation of the final product in pseudo-steady-state is equal to the rate of consumption of the initial agent *A*, obtain the overall rate for the reaction:

**( 10)**
$$\frac{d[A]}{dt} = -K_{1f}[A][B] + K_{1b}\frac{K_{1f}[A][B]}{K_{1b}[M] + K_2} = [A][B]K_{1f}\left[\frac{K_{1b}}{K_{1b} + K_2[M]} - 1\right] =$$
$$= -\frac{K_{1f}K_2[M]}{K_{1b} + K_2[M]}[A][B]$$

This means that the overall reaction rate depends on concentration of the background species *M*. In case of very high concentration of *M*, the value of $K_2$ in denominator can be neglected, which leads to *M*-independent reaction rate $K_{1f}K_2 / K_{1b}$. To the opposite, in case of low *M* concentrations, the $K_2$ in denominator is dominant and the reaction rate becomes linearly proportional to *[M]*.

The equation ( 10) is called the Lindemann-Hinshelwood rate expression, which is based, in particular, on the assumption that one single collision with the third-body molecule is enough to take out the excess of energy. In real life, one single collision with the third body is rarely enough to stabilise the reaction product. Therefore, in 1983 Troe developed an experimentally better-fitting equation for the rate. Using more common notations for the coefficients, it can be written as:

$$K(T) = \frac{K_0 K_\infty [M]}{K_\infty + K_0[M]} F^R, \ \ where \ \ R = \left( 1 + \left[ \log_{10} \frac{K_0[M]}{K_\infty} \right]^2 \right)^{-1} \tag{ 11}$$

This modified form fits well most of the experimental data.

Note that termolecular reactions often exhibit decreasing rate with increasing temperature. The higher the temperature the bigger the kinetic energy of the reactants and the larger the internal vibrational energy stored in the intermediate excited product. Hence, the probability of its breakout to initial constituents is also higher.

### Examples of simplification of the chemical reaction chains

Simple examples allowing for straightforward simplifications of the equations are:

1. If one of the two sequential reactions is substantially faster, its dynamics can be neglected and the final products considered as created instantly.
2. If one of the two agents is in substantially larger concentrations, the reaction order can be reduced by including its concentration into the rate coefficient.
3. Life time of the agent in lack is defined via the first-order differential equation.

Less trivial is the concept of chemical family. Let's consider three species *A*, *B*, *C*, which are connected via the following reactions:

$$A + B \xleftrightarrow{K_f,\, K_b} AB \xrightarrow{K_3} C \tag{ 12}$$

Let also the forward and inverse reactions rates $K_f$ and $K_b$ are much higher than $K_2$. In this case, *A* and *B* are practically always in equilibrium and can be considered together as a family $A_x$. Taking into account the sources of both *A* and *B*, one can write down the equations for all the species:

$$\frac{d[A]}{dt} = -K_f[A] + K_b[B] + S_A$$

$$\frac{d[B]}{dt} = K_f[A] - K_b[B] - K_3[B] + S_B$$

$$\frac{d[C]}{dt} = K_3[B]$$

$$\frac{d\,[A_x]}{dt} = \frac{d([A]+[B])}{dt} = -K_3[B] + S_A + S_B$$

Solution for stationary concentrations of *A* and *B* evidently leads to:

$$[B] = \frac{S_A + S_B}{K_3}$$

$$[A] = \frac{K_b}{K_f\, K_3}(S_A + S_B) + \frac{S_A}{K_f}$$

$$\frac{[A]}{[B]} = \frac{K_b}{K_f} + \frac{S_A}{K_f}\frac{K_3}{S_A + S_B}$$

In absence of the sources, fast rates $K_f$, $K_b$ of the reversible reaction imply that $K_f[A] \approx K_b[B]$. It is also evident that the overall equilibrium of the family $A_x$ implies balance of sources and the sink, i.e. $K_3[B]=S_A+S_B$.

## Examples of chemical transformation chains in the troposphere

### Major oxidants in the atmosphere: OH, $O_3$, $NO_3$, $HO_2$

The most important oxidants in the troposphere and, more generally, in the atmosphere, are OH and $O_3$, with significant contribution of $NO_3$ at might time and $HO_2$ taking part in the ozone formation. Essentially, these four agents are responsible for most of the chemical transformation processes in the atmosphere.

Main pathway of OH formation is via ozone photolysis with the following hydrolysis of the excited oxygen atom.

**( 13)**

$$\begin{aligned} &O_3 \xrightarrow{h\nu} O(^1D) + O_2 \\ &O(^1D) \xrightarrow{M} O_3 \\ &O(^1D) + H_2O \to 2OH \end{aligned}$$

The fraction of the excited $O(^1D)$ atoms forming OH is quite small. Thus, at normal pressure and relative humidity RH=50% only 10% of the photolysed ozone leads to formation of OH radical, the rest falls back to ozone. Ozone photolysis rate at the surface in midday at the tropics in clear-sky conditions is about 5 $10^{-5}$ $sec^{-1}$.

Other regionally important sources, especially in the polluted atmosphere, are photolysis of nitrous acid HONO and hydrogen peroxide $H_2O_2$:

**( 14)**

$$\begin{aligned} &HONO \xrightarrow{h\nu} NO + OH \\ &H_2O_2 \xrightarrow{h\nu} 2OH \end{aligned}$$

The above reactions, being probably the most important sources of OH, are not the only ones that are responsible for its formation. Due to their high reactivity, concentration of the OH radicals in the atmosphere is so low that virtually any single oxidation reaction involving OH would result in their almost immediate disappearance. Let's consider the production chain ( 13) and the loss of OH for the oxidation of methane $CH_4$. The methane concentration is quite stable and uniformly distributed gas. Time trend exists but amounts for a few % per year – the $CH_4$ level has approximately doubled over the last hundred years.

The methane oxidation follows the typical scheme:

$$CH_4 + OH \xrightarrow{\mathrm{O_2,\ \ 1.48e6*exp(-1775./T)}} CH_3O_2 + H_2O$$

where the reaction rate is given in [$\mathrm{sec}^{-1}$ $\mathrm{mole}^{-1}$ $\mathrm{m}^3$].

Assuming the methane concentrations to be 1650 ppb ~ 70 μmole $\mathrm{m}^{-3}$ and the oxidation rate at T=300K to be ~4 $10^3$ $\mathrm{sec}^{-1}$ $\mathrm{m}^3$ $\mathrm{mole}^{-1}$ one cam obtain the expected life time of OH with regard to methane oxidation: $\tau \sim (7\ 10^{-5} * 4\ 10^3)^{-1}\ \sec \approx 3.5 \sec$.

The reason why OH is not disappearing is that every reaction chain using it up is followed or preceded by another reaction forming either OH or $HO_2$, which then reacts with NO or other agents returning OH radical.

Since most of the OH formation processes are photolytic, it is important mainly during daytime, with night-time concentrations being about 100 times lower than those during day. Atmospheric transport of OH radicals is unimportant due to their extremely fast chemical cycling.

The only known significant source of ozone in the troposphere is photolysis of $NO_2$:

**( 15)**

$$NO_2 \xrightarrow{h\nu} NO + O(^3P)$$
$$O(^3P) + O_2 \xrightarrow{M} O_3$$

Ozone is a sufficiently long-living species, which can easily survive for several hours, which makes it one of the important night-time oxidants.

The nitrate radical is formed in the reaction of $NO_2$ and ozone:

**( 16)**

$$NO_2 + O_3 \rightarrow NO_3 + O_2$$

Due to its fast photolysitic decomposition, nitrate radical is present in substantial concentrations only during night time.

Production chains of $HO_2$ radical are numerous but generally include the reaction leaving an isolated hydrogen atom or HCO radical, which immediately react with oxygen forming peroxy radical:

$$HCO + O_2 \rightarrow HO_2 + CO$$
$$H + O_2 \rightarrow HO_2$$

For example, photolysis of formaldehyde HCHO leads to intensive formation of $HO_2$:

$$HCHO \xrightarrow{h\nu} H + HCO$$

### Examples of some major tropospheric chemical branches

### Sulphur dioxide

The set of reactions starting from sulphur dioxide ultimately leads to formation of sulphates, along side with several other products. In typical conditions, the oxidation can follow via two pathways: gas- and liquid- phase oxidation chains.

The gas-phase chain, as well as many other oxidation chains, starts from attack of OH radical:

$$SO_2 + OH \rightarrow HOSO_2 \xrightarrow{M,\ O_2} HO_2 + SO_3$$
$$H_2O + SO_3 \rightarrow H_2SO_4 \rightarrow particulate\ \ form,\ sulphates$$

Importantly, this chain demonstrates the cycling of OH and $HO_2$, where the OH-consuming reaction is followed by the other one (fast!), which produces $HO_2$, leaving the restoration of OH to another quick reactions with NO or other active agents. It is also worth mentioning that the presence of water is crucial for the final stage of the transformation branch.

The heterogeneous chain starts from dissolution of $SO_2$ in a water droplet of fog or cloud:

$$SO_2(g) + H_2O \leftrightarrow SO_2 \cdot H_2O(aq)$$
$$SO_2 \cdot H_2O \leftrightarrow HSO_3^- + H^+$$
$$HSO_3^- \leftrightarrow SO_3^= + H^+$$

Upon dissolution, the mixture of $SO_2$ $H_2O$, $HSO_3^-$, and $SO_3^=$ is oxidised by (i) ozone, (ii) oxygen, and (iii) hydrogen peroxide $H_2O_2$ dissolved in water. The processes are numerous and their detailed consideration is beyond this course. It is only worth mentioning that the liquid-phase oxidation largely depends on pH of water and presence of catalytic agents, such as $Fe^{3+}$ or $Mn^{2+}$.

The considered set of oxidation of sulphur dioxide is accepted to be largely responsible for acid rains and acid deposition environmental problem.

### Basic photochemical cycle

Arguably the most-important set of reactions is associated with formation of the tropospheric ozone, which is one of the major components in photochemical smog.

Due to a potentially huge number of reactions involved into the consideration, we will limit the analysis with a few simplified cases.

The core of the photochemical ozone production and destruction is a set of three reactions:

**( 17)**

$$NO + O_3 \rightarrow NO_2 + O_2$$

**( 18)**

$$NO_2 \xrightarrow{h\nu,\ O2} NO + O_3$$

**( 19)**

$$O3 \xrightarrow{h\nu} O + O_2$$

In differential form, these read:

**( 20)**

$$\frac{d[O_3]}{dt} = j_{NO2}[NO_2] - k_{NO\_o3}[NO][O_3] - j_{O3}[O_3]$$

**( 21)**

$$\frac{d[NO_2]}{dt} = -j_{NO2}[NO_2] + k_{NO\_o3}[NO][O_3]$$

**( 22)**

$$\frac{d[NO]}{dt} = -\frac{d[NO_2]}{dt}$$

This set of equations has a stationary equilibrium solution, which we will obtain under a simplifying assumption that the photodissociation destruction of ozone is much slower than the equilibrium establishment (well fulfilled in actual conditions). Then the reaction ( 19) can be neglected and the last term in ( 20) disappears.

We also have to invoke the mass budget consideration, which connect the initial and final amounts of NOx.

**( 23)**

$$\begin{gathered}[NO]_0 + [NO_2]_0 = [NO] + [NO_2] \\ [O3] - [O3]_0 = [NO] - [NO]_0\end{gathered}$$

Then:

**( 24)**

$$\begin{aligned}[O_3] &= \frac{j_{NO2}[NO_2]}{k_{NO\_o3}[NO]} = \\ &= \frac{1}{2}\left\{[O_3]_0 - [NO]_0 - \frac{j_{NO2}}{k_{NO\_o3}} + \sqrt{\left([O_3]_0 - [NO]_0 - \frac{j_{NO2}}{k_{NO\_o3}}\right)^2 + 4\frac{j_{NO2}}{k_{NO\_o3}}([NO_2]_0 + [O_3]_0)}\right\}\end{aligned}$$

After that, the concentrations for NO and $NO_2$ are obtained from budget equations ( 23).

As one can see, the final ozone concentration is growing with availability of $NO_2$ while NO is reducing it. For very high $NO_2$, the equilibrium ozone concentrations are approximately proportional to square root of initial $NO_2$. In case of sufficiently large NO concentrations, ozone can be consumed almost entirely.

The above situation, being transparent and easy for the analysis, never occurs in reality. The main reason for that is presence of other branches of the chemical transformations converting NO to $NO_2$. As follows from ( 18), creation of $NO_2$ concentration above the photostationary equilibrium ( 23)-( 24) leads to formation of extra ozone while the system returns to the equilibrium.

The most-common template of the reactions converting NO to $NO_2$ without consuming ozone is the following.

**( 25)**

$$\begin{gathered}RH + OH \xrightarrow{O2} RO_2 + H_2O \\ RO_2 + NO \rightarrow NO_2 + products\end{gathered}$$

Here *R* denotes an organic radical, for example: $CH_3$-, $C_2H_5$-, etc. In fact, even $HO_2$ can be included into this list.

The first reaction in the chain ( 25) is usually slow in comparison with the second one.

The $RO_2$ radicals also play several roles, apart from the NO oxidation, which creates competing branches to the ozone-producing one.

Accounting for the $RO_2$ agent leads to modification of the equation ( 21) and adds one more to the system:

**( 26)**

$$\frac{d[NO_2]}{dt} = -j_{NO2}[NO_2] + k_{NO\_o3}[NO][O_3] + k_{NO\_RO2}[NO][RO_2]$$

**( 27)**

$$\frac{d[RO_2]}{dt} = pRO_2 - k_{NO\_RO2}[NO][RO_2]$$

Here $pRO_2$ is an overall production term of the $RO_2$ agent: oxidation of RH with the OH radical may be not the only way producing it.

Analysis of the system of equations ( 20), ( 22), ( 26), ( 27) is not trivial and in general case cannot be done analytically. Some specific situations, however, can still be considered.

Let’s assume that concentration of the $RO_2$ agent is constant for any level of $NO$. This is not too unrealistic because of competing branches destroying the excess of $RO_2$, as well as due to its stable supply from usually large reservoir of $RH$. Under this assumption, let’s consider several specific cases.

Case 1. Ozone concentrations correspond to the photostationary equilibrium ( 24). From ( 26): $d(NO_2)/dt > 0$, i.e. the equilibrium will be broken towards further growth of ozone and $NO_2$.

Case 2. Since in the case 1 the photostationary equilibrium does not stay due to the system migrating towards higher $NO_2$, let’s consider what happens when $NO_2 \sim NOx$ and $NO \sim 0$. From ( 26), $d(NO_2)/dt < 0$, i.e. the excess of $NO_2$ will be photolysed reducing its concentration and stabilising the system. However, the equilibrium is not possible. Indeed, is assuming $d(NO_2)/dt = 0$, from ( 20), again neglecting slow ozone photolysis, obtain that ozone continues to grow: $d(O_3)/dt = k_{RO2\_NO}[NO][RO_2]$, which will lead to further reduction of $NO$ and growth of $NO_2$.

Case 3. As it is seen from the above cases, the system tends to create an unlimited amount of ozone using-up $RO_2$ gradually increasing $NO_2$ and reducing $NO$. If allowing the process to go long enough, the direct dependence of $NO$ and $O_3$ can show up and the initial conditions will be forgotten.

# Removal processes

There are two types of the removal mechanisms generally considered in the atmospheric composition modelling: dry deposition and scavenging with precipitation (often also called as wet deposition). Physical processes behind these mechanisms are strongly different, still under certain conditions resembling strong similarities with each other. Below the background of both of these mechanisms is considered and related back to the underlying features of gases and liquids.

## *Derivation of the diffusion parameters from the molecular-kinetic theory*

Since the diffusion processes play the crucial role in both removal mechanisms, it is convenient to recall some of the key features and parameters of molecular diffusion using simplified considerations of molecular kinematic theory.

### Mean free-run path length in gas/liquid

Let’s consider a gas molecule with own diameter $d$. A condition of its collision with another molecule is that the distance between the molecule centres is less than $2d$. Let’s assume that the collision is non-dissipative, i.e. the total kinetic energy of colliding molecules does not change due to the collision. Let’s then consider the path on a molecule, which consists of a set of straight lines between the collisions and sudden changes of speed and direction at each collision. Also, let this be the only moving molecule while the others are motionless. Finally, let’s consider the sphere with the diameter $2d$ centred around the moving molecule. Denote the total volume of a broken cylinder drawn by this sphere while the molecule is in motion be $V$. Let the free-run lines are much larger than the molecule diameter $d$. Then the breakpoints do not change the cylinder volume, which will be simply:

$$V = \pi d^2 v\tau = \sigma v\tau$$

Here $\sigma$ is the cross-section of the 2d-sphere, $v$ is the mean velocity of the molecule and $\tau$ is time interval.

Then the number of collisions is equal to the number of molecules located in the volume $V$.

$$N_c = nV = n\sigma v\tau\,,$$

where $n$ is the gas number-density. The total path passed by the molecule during this time period is $v\tau$. Then the mean length of the free-run path will be:

**( 28)**
$$\lambda = \frac{v\tau}{N_c} = \frac{1}{n\sigma}$$

With all the crudeness of the above consideration, the obtained relation is pretty accurate and gives good approximation of the actual free-run path estimate.

A more rigorous consideration leading to correct estimate has to take into account movements of the other molecules as well. From mechanics it is known that 2-body collision with masses $m_1$ and $m_2$ can be considered with the coordinate system connected with one of the bodies, which is then motionless. However, the mass of the second body should be replaced with:

**( 29)**
$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

Since time of collision remained the same, so as forces pushing the molecule, the relative speed is larger than the absolute one with a factor $\sqrt{m/\mu}$ (energy is proportional to square of the speed). For $m_1=m_2$ this leads to $v_{relat} = v\sqrt{2}$ and:

**( 30)**
$$\lambda_{exact} = \frac{1}{\sqrt{2}\,n\sigma}\,,$$

which coincides with rigorous calculation of Maxwell.

For the case of two different gases, one has to involve the requirement of the temperature equality for the both gasses in the mixture: $m_1 v_1^2 = m_2 v_2^2$. Then:

**( 31)**
$$v_{relat} = v_1\sqrt{m_1/\mu} = \sqrt{v_1^2 + v_2^2}$$

Then the number of collisions of the molecule of the type 1 with the molecules of the type 2 will become:

$$N_c = n_2\sigma_{12}\sqrt{v_1^2 + v_2^2}\,, \qquad \sigma_{12} = \pi(r_1^2 + r_2^2)$$

Finally, the free-run path of the molecule 1 due to collisions with the molecule type 2 is:

**( 32)**
$$\lambda_{exact} = \frac{1}{n_2\sigma_{12}\sqrt{1 + v_2^2/v_1^2}} = \frac{1}{n_2\sigma_{12}\sqrt{1 + m_1/m_2}}$$

## Molecular diffusivity. Einstein formula

Let now assume that the molecules of the type 1 are under some regular force $F$ (or any type: gravitational, electro-magnetic, …). Then they will start moving through the gas 2 with some regular mean velocity $\boldsymbol{u}$. The proportionality coefficient between $\boldsymbol{\Phi}$ and $u$ is called as the molecular diffusivity $B$: $\boldsymbol{u}=B\boldsymbol{\Phi}$.

Evidently, in such case there will be an accumulation of the molecules of gas 1 downstream of the force $\boldsymbol{\Phi}$. The potential energy of the molecules due to this force will be evidently $E= -Fx$ (x-axis direction coincides with $\boldsymbol{\Phi}$). Then, according to Boltzmann's law, the distribution of the molecules in space will be the following:

$$n = n_0 e^{-E/kT} = n_0 e^{\Phi x/kT}$$

Such distribution has the gradient of the concentration, which will cause the diffusion flux. In the stationary case these two fluxes will be identical and mutually compensating. Projecting them to x-axis, one obtains the stationarity condition:

$$-D\frac{dn}{dx} + \Phi B n = 0$$

Here $D$ is the diffusion coefficient of the gas 1 through the gas 2. From where it follows that:

**( 33)** $$D = kTB$$

This connection between the diffusion coefficient and the molecular diffusivity has been established by Einstein and named after him.

## Connection of micro- and macro- parameters for the gas diffusion

Let's consider the mutual diffusion of gas 1 and gas 2 through each other assuming that the thermodynamically these are in equilibrium (temperature and the total concentration $n$ are constant in the whole volume: $n_1+n_2=n=const$). Let's compute the diffusivity of these gases from the macro-parameters of the experiment.

The diffusion fluxes will be:

$$F_1 = -D_{12}\frac{dn_1}{dx}, \quad F_2 = -D_{21}\frac{dn_2}{dx}$$

Such flux implies a certain regular mean velocity of the molecules (apart from zero-mean heat-induced one). That requires a certain force to support it. Finding this force will solve the problem. Let's consider the single molecule of type 1, which has the non-zero mean velocity $u_1$ (heat-induced fluctuations are neglected as they are zero-mean). The collision of this molecule with the other ones of gas 1 are of zero mean as well as they all are moving in the same direction with the same mean speed. Then the collisions with molecules of gas 2 are the only ones compensating the driving force. The molecules 2 also have heat-induced and regular components, where the first one can be neglected as zero-mean. Therefore, the problem is reduced to the a collision of two molecules with velocities $u_1$ and $u_2$. The centre of mass of these molecules moves with

$$V = \frac{m_1 u_1 + m_2 u_2}{m_1 + m_2}$$

In case of ideal non-dissipating collision, in the coordinate system connected with the centre of masses, the mean velocities after the strike are zero (the reflection is symmetrical). Then, in the laboratory system the mean velocities will be both $V$. Then the change of velocity of the molecule 1 due to collision will be

$$\langle \Delta u_1 \rangle = V - u_1 = \frac{m_2(u_2 - u_1)}{m_1 + m_2}$$

Then the total force acting on the molecule will be the change of the momentum in a single collision multiplied with the number of collisions per unit time:

$$\Phi_1 = N_{12} \frac{m_1 m_2 (u_2 - u_1)}{m_1 + m_2} = N_{12} \mu (u_2 - u_1)$$

The requirement of constant total density of the mixture leads to: $n_1 u_1 + n_2 u_2 = 0$. Then:

( 34)
$$\Phi_1 = \frac{n}{n_2} N_{12} \mu u_1,$$
$$B_1 = \frac{n_2}{n N_{12} \mu u_1} = \frac{1}{n \sigma_{12} \mu \sqrt{v_1^2 + v_2^2}},$$
$$D_{12} = D_{21} = \frac{kT}{n \sigma_{12} \mu \sqrt{v_1^2 + v_2^2}}$$

Note that the diffusivity and diffusion coefficients do not depend on actual concentrations of the gases but only on their total concentration, mutual cross-section, and relations between their masses and heat-induced velocities.

## Viscosity and heat condactivity

In the section 1, the equation for the closure of the turbulent diffusion equation has been derived using the mixing-length assumption. The same consideration passes for molecular diffusion, which can transport the concentration, momentum or heat. The only difference will be that instead of mixing length distance one has to consider the free-run path length, which has been derived above.

Using the above notations, in presence of a gradient of the mean velocity along x-axis, the mean momentum flux across the axis will be

$$G = -\alpha\, n\, m\, v \lambda \frac{du}{dx}$$

Here $\alpha$=1/3 is numerical coefficient, *n* is the gas density, *m* is its molecular mass, *v* is the mean heat-induced velocity and $\lambda$ is the free-run path length.

This momentum flux corresponds to viscous stress:

( 35)
$$\tau_{xy} = -\alpha\, n\, m\, v \lambda \frac{du}{dx} = -\eta \frac{du}{dx}, \quad \eta = \alpha\, n\, m\, v \lambda = \alpha\, \rho\, v \lambda$$

Analogously, the heat flux due to molecular diffusion will be:

( 36)
$$q = -\alpha\, n\, m\, v \lambda\, c_v \frac{dT}{dx} = -k \frac{du}{dx}, \quad k = \alpha\, n\, m\, v \lambda c_v = \alpha\, \rho\, v \lambda\, c_v$$

Interestingly, ( 36) and ( 38) imply that the ratio between viscocity and heat condactivity is just the heat capacity $c_v$. Experimentally, it is somewhat more general:

( 37)
$$\frac{k}{\eta} = A c_v$$

where A~2-2.5 depending on the rotational features of the particular molecules.

The second non-trivial observation is that, with the free-run length $\lambda$ being inversely proportional to the gas density (see ( 32)), neither viscosity nor heat conductivity are dependent on it. This seemingly paradoxical finding has been confirmed by a set of experiments, which highlighted two competing processes: the distance of the unit transfer and the number of these small transfers per time unit, the first being inversely proportional and the second being directly proportional to density of the gas. These two compensate each other, which leads to the absence of the overall dependence.

With the above background (albeit grossly simplified), one can consider the deposition processes and the underlying physics.

## *Dry deposition*

The dry deposition process is generally associated with diffusion and forced transport through a viscous liquid, the latter being responsible for gravitational sedimentation of particles.

The dry deposition term is usually introduced into the advection-diffusion equation as a boundary condition at the lower boundary (surface) and is described via a dynamic coefficient with a dimension of speed [m sec$^{-1}$], usually called as dry deposition velocity $V_d$. (see part 1 of the course).

**( 38)**
$$K_z \frac{\partial C}{\partial z} = C(z_1)\, V_d = F_d$$

Here $z_1$ is the lowest model level for which the prognostic variables are computed. This level is also the reference height for the eddy diffusivity $K_z$ and vertical concentration gradient.

Evaluation of $V_d$ is usually performed under the assumption that no sources of sinks are located below $z_1$, i.e. $F_d$ is constant from $z_1$ down to the ground.

Analyzing the physical processes driving the diffusion down to the surface, one can distinguish three main regions along the vertical axis: (i) turbulent diffusion down to very near the surface (some small height $z_0$ usually called as roughness length), (ii) penetration through the thin air layer immediately adjacent to the surface, and (iii) actual uptake of the tracer by the surface (if several types of the surface are available, the corresponding fluxes have to be summed-up).

Under the constant-flux assumption, it is natural to consider the parameterization in finite-differences terms rather than the differential ones:

**( 39)**
$$F_d = (C(z_1) - C(z_0))V_d^a = (C(z_0) - C(z_{srf}))V_d^b = (C(z_{srf}) - C')V_d^s$$

Here the velocities with super-scripts $a$, $b$, $s$ correspond to the above aerodynamic, quasi-laminar and surface ranges with the corresponding concentrations and their borders.

Equation ( 39) exactly corresponds to the one describing the flow of electric current through the resistances $R_i$, $i=a,b,s$. In more general terms, under the constant-flux assumption, the flux through each diffusion pathway, providing that it is described in a way similar to ( 39), is mathematically identical to equation for the electric current flowing through the corresponding resistance and concentration considered as the electric potential. This similarity is called as a resistance analogy for the dry deposition computation.

The resistance analogy, being just a trivial replacement of the terms at the beginning, brings about a substantial set of mathematical tools for the flow analysis. For instance, the diffusion flux (i.e. the current) can be expressed via the Ohm's law:

**( 40)** $$I = U / R, \quad where \quad I \equiv F, \quad U \equiv C(z_2) - C(z_1), \quad R \equiv V_d^{-1}$$

Analysis of multi-pathways schemes can be simplified with two Kirchhoff's laws:

- for every circuit mesh the sum of in- and out- going currents is equal to zero
- for every closed contour with no crossing wire lines, the sum of difference of potentials at each resistances is equal to the sum of impedances in the contour.

Note that for both Kichgoff's laws the sign of the current is considered positive if it flows into the mesh in question or if it flows in the same direction as the one selected for the contour analysis.

From these tree laws, one can easily derive the rules for sequential or parallel combinations of the resistances and the corresponding equations for the current flows and the difference of potentials.

The resistance analogy becomes particularly convenient for the analysis of the surface uptake of gases, where numerous paths and types of accumulation can be considered, so that the direct analysis of the differential equations becomes bulky (see S&P, section 19.5 as an example). After decomposition, however, each resistance can be either directly measured in the laboratory conditions or derived from semi-empirical theories, which take into account both chemical features of the tracer and the type and state of the particular surface.

Consideration of the atmospheric resistances $R_a$ and $R_b$ can rely on the basic considerations.

## Aerodynamic resistance *Ra*

As shown in the part 1 of the lectures notes, the mean $K_z$ for the thick constant-flux layer from $z_0$ till $z_1$ can be expressed as follows:

$$\overline{K_z} = \left( \int_{z0}^{z1} \frac{dz}{K_z} \right)^{-1}$$

For thermally neutral stratification, the eddy diffusivity is proportional to the maximum size of the eddies, which, in turn, are limited with the distance to the surface, i.e. $K_z \sim z$ or, introducing the dimensionless proportionality coefficient (von Karman constant, $\kappa \sim 0.4$) and velocity scaling (friction velocity, $u^*$):

$$K_z = \kappa u^* z$$

Then the resistance can be evaluated analytically:

$$R_a = \frac{1}{\kappa u^*} \ln(z_1 / z_0)$$

In more general case, empirical correction functions have to be introduced. One of possible shapes of such functions is given by S&P (pg. 907), which also allow the analytical expressions for $R_a$.

## Quasi-laminar resistance *Rb*

This is one of the uncertain parameters, mainly due to ambiguous definition of the roughness length for each particular type of surface. It is generally accepted that every element of the surface roughness has the own thin laminar layer, with its "inner" part sticking to the surface obstacle and the outer one following the movement of the outside air flows.

### Gases

From a general point of view, for gases, the only mechanism of passing through the layer is molecular diffusion, which must be proportional to the diffusivity of the corresponding molecules $D$ and inversely proportional to the kinematic viscosity of air $\nu$. The thickness of the layer itself depends on turbulent stress of the surface, i.e. has to be related to friction velocity $u*$. The only combination of these parameters with right dimension is the following:

**( 41)**
$$R_b = a\frac{Sc^{2/3}}{u*} = a\frac{(\nu / D)^{2/3}}{u*}$$

The dimensionless coefficient $a$ has been experimentally found to be ~5.

### Particles

For particulate tracers there are three mechanisms responsible for the dry deposition: (i) diffusive pathway, (ii) inertial penetration, often referred as impaction mechanism, and (iii) interception mechanism. All three mechanisms are again related to the thickness of the layer, thus they all have to be related to $u*$. It is also convenient to assume that the surface resistance is zero for aerosols but instead there is a certain fraction of particles that stick to the surface once having touched it. Then the overall $R_b$ resistance will be:

**( 42)**
$$R_b = \left(a\ fu*(v_B + v_{\mathrm{Im}} + v_{Int})\right)^{-1}$$

The fraction of particles sticking to the surface is quite close to 1 for fine aerosols but can be somewhat lower if particles have enough inertia to rebound after the collision with the surface. The measure of the inertia in comparison with the surrounding liquid viscosity is described by the Stokes number:

**( 43)**
$$St = \frac{v_s u*^2}{g\nu}$$

Note that here the measure of the particle inertia is represented by its sedimentation velocity $v_s$, which will be discussed further. Empirical studies suggest that the square root of this number is a reasonable description of the fraction of rebound particles. For small ones it goes to zero.

For Brownian mechanism, similar formulations as for gases ( 41) can be involved, with appropriate corrections owing to somewhat different scales and mechanisms of molecular diffusion and Brownian movement:

**( 44)**
$$v_b = Sc^{-\gamma} = \left(\frac{D}{\nu}\right)^{-\gamma},\ \ D = \frac{kT}{3\pi\mu D_p}C_c$$

Here $\gamma$ varies between 1/2 and 2/3, with larger values attributed to rougher surfaces, $D$ is the Brownian diffusivity, and $C_c$ is a so-called no-slip correction introduced for the very small particles whose size is less than the free-run path of the surrounding gas molecules. Comparison of ( 33) - ( 34) for molecular diffusion, from one side and ( 44) for Brownian diffusion from another reveals the similarities between the underlying processes.

Impaction corresponds to inertial penetration, which can be described in terms of a ratio of the depth of the laminar layer and the distance at which the particle velocity gets relaxed towards the surrounding liquid. A semi-empirical model of Zhang et al (see S&P, pg.910) suggests:

( 45) $$v_{im} = \left( \frac{St}{y + St} \right)^2$$

Here *y* depends on land-use category.

Finally, the interseption mechanism depends almost exclusively on the ratio of the particles and the characteristic size of the obstacles.

Combining the above terms, one can obtain the following estimate for $R_b$:

( 46) $$R_b = \left\{ 3u * e^{-\sqrt{St}} \left( Sc^{-\gamma} + \left( \frac{St}{y + St} \right)^2 + 0.5 \left( \frac{D_p}{A} \right)^2 \right) \right\}^{-1}$$

## Surface resistance *R<sub>s</sub>*

Detailed consideration of the surface resistance lies outside the current course due to almost entirely empirical character of the corresponding parameterizations. Here it is only worth mentioning that for the aerosol compounds it is assumed to be zero, while for gases it depends on type of the surface, type and state of vegetation, humidity of the surface and chemical and physical features of the tracer in question. More information can be found in S&P, p.912 and further.

## Gravitational sedimentation of aerosol particles

Let us consider the particle moving under the gravitational force. According to the Brownian diffusivity formula ( 44), it will define the mean stationary velocity of the particle. The corresponding drag force has been derived by Stokes and has its name:

( 47) $$m \frac{dv}{dt} = mg - F_{Stokes} = mg - 3\pi D_p \mu v C_c^{-1}$$

where *m* is the mass of the particle and *g* is gravitational acceleration.

Then the stationary sedimentation speed will be:

( 48) $$v_s = \frac{mg}{3\pi D_p \mu} C_c = \frac{\rho D_p^2 g}{18\pi \mu} C_c$$

Let now consider the very widely used representation of the gravitational sedimentation process within the scope of resistance analogy. According to that, the sedimentation flux should be the product of the concentration at the reference height multiplied with the sedimentation velocity. This resistance is then parallel to the sequential cascade of the $R_a$ and $R_b$. Applying the Kirchhoff's rules, one can easily obtain:

( 49) $$R_{dd}^{-1} = R_s^{-1} + (R_a + R_b)^{-1} = v_s + (R_a + R_b)^{-1}$$

However, this formula directly contradicts to another one, widely used in the literature and models:

( 50) $$R_{dd}^{-1} = v_s + (R_a + R_b + R_a R_b v_s)^{-1}$$

The later formula is derived without any formal considerations of the resistances but rather from the constant-flux assumption:

$$F = \frac{C_{z1} - C_{z0}}{R_a} + v_s C_{z1} = \frac{C_{z0}}{R_b} + v_s C_{z0} = \frac{C_{z1}}{R_{dd}}$$

This illustration shows the problem in applying the resistance analogy – essentially the description of flows due to difference of two generic potentials at two points – in the case when the flow is determined by externally decided velocity and concentration of the species.

## Wet deposition

Scavenging with precipitation is a very complicated process with limited possibilities to study it in analytically. In most cases, the scavenging coefficients are measured in field or laboratory conditions and then interpreted in terms of the processes that are assumed to drive the observed dependencies. In the end, the parameterization is reduced to the scavenging coefficient Λ, which defines the rate of the removal:

**( 51)**

$$\frac{dC}{dt} - -\Lambda C$$

This coefficient depends on virtually all imaginable parameters: type of precipitation, its intensity, droplet/snowflake size, electric phenomena, tracer chemical and physical properties, solubility, pH of the precipitation, etc. Some of the features are inter-connected and can dynamically change during the fall of the specific droplet.

Therefore, below only a short outline of the main driving forces and corresponding links are given.

Scavenging is usually split to in-cloud and sub-cloud parts. The main difference is in dynamic of the droplet population: inside the cloud the droplets grow, while during the free-fall towards surface they tend to evaporate. For scavenging of particles, an additional dimension of complexity is the particle inertia, which results in “wiping” effect when the falling droplet cleans the entire underlying column or its part from aerosols.

Usually reasonable estimate of the scavenging efficiency of soluble gases (for both in- and sub-cloud scavenging) comes from the following basic equation:

**( 52)**

$$\frac{dC_{aq}}{dt} = K_c(C_g - C_{eq}) = K_c(C_g - \frac{C_{aq}}{HRT})$$

Here $K_c$ is the mass transfer coefficient between the gaseous and aqueous phases, $C_g$ is the gas-phase concentration of the tracer (denoted as $C$ in the above chapters), $C_{aq}$ is the concentration in the aqueous phase, $H$ is the equivalent Henri’s law constant, R is universal gas constant, $T$ is temperature. The main complexity is now split between two coefficients: the Henri’s law constant describing the solubility of specific tracer in stationary conditions, and the mass transfer coefficient $K_c$, which describes the dynamics of the solution process.