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## SPREADING OF A SATURATION FRONT OF HETEROGENEOUS CHEMICAL REACTION THROUGH AN AEROSOL CLOUD

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**Abstract.** A cloud of aerosol particles sediments in air containing reactants. On the basis of a macroscopic chemical and mass transfer model founded on the kinetic theory of heterogeneous reactions we analyzed the spreading of chemical reaction through the cloud of aerosol particles. In this paper we considered a binary reaction with one volatile and one non-volatile product at the surface of aerosol particles. If the finite saturation capacity with respect to non-volatile reaction product accumulated in the droplet is taken into account, the eventual deceleration of the reaction results in the propagation of a saturation front. The spatial distributions of concentrations and their evolution in time are determined, as well as the velocity of saturation front.

**Key words:** aerosol, droplet, heterogeneous chemical reaction, mass transfer.

**1. Introduction.** Heterogeneous chemical reactions are known to play an important role in a wide class of geophysical phenomena, including atmospheric processes [1]. This was first recognized in the late 1970s for the production of  $H_2SO_4$  and  $HNO_3$  in acid rain [2]. Their critical role for the depletion of stratospheric  $O_3$  was established in the late 1980s [3]. While the "homogeneous" chemistry of most of the processes is quite well understood, their «heterogeneous» counterparts still remain the subject of considerable debate (see, e.g., [3], pp. 216-229). The term «heterogeneous» is used both for true heterogeneous reactions taking place at the surface of a particle or a liquid droplet and for the reactions that occur homogeneously in the dispersed condensed phase [1]. In the present work we consider the former type.

The theory of heterogeneous reactions of gas with individual liquid droplets is considered in many papers [4–6] and books [7] and [8]. This overall process includes several steps: mass transfer of reacting species in gaseous phase, adsorption or/and mass transport across the aerosol surface, chemical reaction at the surface, mass transport and the chemical reaction within the liquid droplets, possible evolution of volatile product species into the gas phase, and subsequent gas-phase mass transport of the evolved gaseous product. Some of the steps may become rate-limiting. In order to evaluate the rate of the overall process one needs to identify such a step (or steps) and to evaluate the rate of such step(s). If the mass-transport processes are essentially faster than the chemical reactions, then the rate of the overall process is governed essentially by chemical kinetics. In the opposite limit, for very fast reactions, the overall process is controlled by the rate of gas-phase mass transport [4].



Investigations in atmospheric physics and chemistry are often aimed at understanding and predicting space-time distributions of reactants and reaction products at macroscopic scales (at the scales much larger than the size of aerosol particles and their mutual distances) which is important for predicting air pollution at regional and global scales as well as for climatology. The importance of heterogeneous atmospheric reaction is now commonly recognized (see e.g. [9] and [8]). The first generation of global multiphase atmospheric models were termed equilibrium models [10,11]. However it was soon recognized [11,12] that no such equilibrium is ever attained. So the problem of treating the time-dependent mass exchange, uptake and production due to chemical reaction arises. The kinetic expressions, once obtained, usually are incorporated into elaborate global models, which include tens of reactants and hundreds of reactions. However, the fully nonlinear description of the chemical kinetics is computationally demanding and often introduces instabilities. Therefore, the treatment of heterogeneous reactions is typically simplified by the assumption of excess of one of the reactants [2,9,13,14].

In the present paper we apply a macroscopic approach proposed in the chemical reactor engineering context by [15–19] to describe the spatial-temporal distribution of reactants and the product for fast binary heterogeneous reactions in a cloud of liquid droplets. The theory has been experimentally validated in two phase liquid-liquid chemical reactors by [20,21]. The treatment here takes into account a second order fast irreversible reaction at the surface of the droplets, overall mass transfer due to bulk convection as well as due to turbulent diffusion. The heterogeneous character of the chemical reaction is taken into account by distinguishing the mean reactant concentration in the bulk fluid and the mean local concentrations at the surfaces of particles as macroscopic variables of the model. The resulting model, which is described in the next section, is non-linear, yet it admits an analysis by approximation theory in closed form. We show below for an example of a single binary heterogeneous reaction, that the reactant which is in a global excess still may be in local (at the reactive surface) deficit in some space-time domains if the local mass transfer between particles and gas phase is taken into account properly. If the finite capacity with respect to non-volatile reaction product accumulated in the droplet is taken into account, the eventual deceleration of the reaction results in the spreading of a saturation front. This qualitative effect is targeted in the present communication. The spatial distributions and their evolution in time of concentrations are determined, as well as the velocity of saturation front. Contrary to the common practice of dealing with a binary heterogeneous reaction, we do not *a priori* assume local excess of one of the reactants. Our analysis reveals coexistence of a spatial domain where one reactant is in local excess with another domain where the other reactant is in excess and the first one is depleted.

We applied our theory to a particular type of reaction where gaseous reactants are distributed in the air, but one of the reaction products is gaseous and the other one is non-volatile. The latter product is soluble and accumulates in the droplets. Reactions of this kind play an important role in the chain of reactions of ozone depletion in polar stratospheric clouds. As an example we considered the binary chemical reaction of chlorine nitrate  $\text{ClONO}_2$  and  $\text{HCl}$  yielding the gaseous product  $\text{Cl}_2$ , and the non-volatile product  $\text{HNO}_3$ . These reactions are well known to be slow in the gaseous phase even at room



temperature; they become feasible only as a result of hydration on the surface of liquid droplets and the formation of ionic intermediates [3]. The particles are assumed to be of the kind normally referred to as polar stratospheric clouds type Ib, that is supercooled ternary  $\text{H}_2\text{SO}_4/\text{HNO}_3/\text{H}_2\text{O}$  solutions. The non volatile product  $\text{HNO}_3$  is taken up by droplets which finally turn into quasi-binary  $\text{HNO}_3/\text{H}_2\text{O}$  droplets with close to 1:3 stoichiometry. This reaction is considered in the literature to be practically irreversible under stratospheric conditions [3].

The paper is organized as follows. In the section 1 we describe the macroscopic model that is applied in the section 3 to study macroscopic dynamics of spatial distributions of concentrations of the reactants and the reaction products when a cloud of liquid droplets sediments in the stratosphere. It is assumed that the binary reaction takes place on the surface of aerosol particles. If the finite solubility capacity of droplets is taken into account, the theory predicts formation of a stationary advancing reaction saturation front. In the section 4 we applied the theoretical results to the above mentioned stratospheric reaction and give numerical estimates for this case. We discuss in the same section the results obtained and the accuracy of approximations. The details of calculations are presented in Appendices A, B, and C.

**2. The model.** We consider an ensemble of identical droplets sedimenting in air with constant velocity determined by the balance of gravitational force and Stokes friction. Premixed reactants  $A_1$  and  $A_2$ , with concentrations  $c_1$  and  $c_2$  react on the surface of the liquid droplets, a single gaseous product  $A_3$  with a concentration  $c_3$  is injected to the air. Since the reaction is fast at the surface of aerosols and is slow in the bulk air, the heterogeneous nature of the reaction should be taken into account and will effect macroscopic dynamics.

At the scale of a single particle both molecular diffusion and convection contribute to the 3-dimensional mass transport between the local gas and the droplet, however, for the particular problem addressed in the present paper, mass transport at the particle scale is approximated by molecular diffusion. Thus the flux densities to/from the surface  $j_i^{(s)}$  are driven by the difference between bulk  $c_i$  and surface  $c_i^{(s)}$  concentrations

$$j_i^{(s)} = \kappa_i \left( c_i - c_i^{(s)} \right) , \quad i = 1, 2, 3, \quad (1)$$

where  $\kappa_i$  are the mass transfer coefficients. The bulk concentrations  $c_i$  are defined as concentrations of reagents and reaction product far away from the aerosol particles (that is at distances much larger than the particle size) and the surface concentrations  $c_i^{(s)}$  are defined as values of the concentrations at the surface of aerosol particles. The difference between bulk and surface concentrations is maintained by chemical reaction at the surface. Concentrations  $c_i$  and  $c_i^{(s)}$  are measured in mole fractions and therefore are non-dimensional.

To determine the fluxes of reactants to the particles, it is necessary to evaluate, in the vicinity of each particle, the distribution of concentrations, which approaches concentration  $c_i^{(s)}$  at the surface and  $c_i$  far from the particle. Implicit in the definition of the mass transfer coefficients  $\kappa_i$ , both molecular diffusion and convection contribute to the mass transport between the local gas and the droplets, which move relative to the surrounding gas. For the particular example which is considered in the present paper, Stokes sedimentation



at low Reynolds and Péclet numbers of the small particles is assumed (see section 4). Equation (1)  $j_i^{(s)}$  follows from the solution of the steady diffusion problem. The overall large-scale gradient introduces slight anisotropy, however for a purely diffusion problem the corresponding corrections will be of the order of the ratio: (particle size)/(scale of the overall gradients). To apply the model to larger particles or faster flow, known correlations for  $\kappa_i$  may be used [6, 6, 7] and [8]. We consider a dilute suspension of droplets following the estimate of the mean ratio of diameter to inter-drop spacing in clouds less than  $10^{-2}$  [4]. Consequently, the local concentration distributions around a particle is unaffected by the presence of other particles.

For binary surface reaction of first order with respect to each reagent, the reaction rate  $R$  is given by the kinetic mass action law:

$$R = k \left( c_1^{(s)} c_2^{(s)} - \frac{1}{K} c_3^{(s)} \right), \quad (2)$$

where  $k$  is the reaction rate coefficient and  $K$  is the equilibrium constant. The latter equation implicitly assumes that the adsorption/desorption kinetics for reagents and product is fast and that it is not rate-limiting. Equation (2) also implies that the relative surface coverage is low. Discussion of the rate (2) is given in the Appendix A). For further discussion see also [19].

The rate of generation of the product at the surface (per unit of surface, per unit of time) equates to the absolute value of the flux density of the volatile product from the surface in a pseudo-steady-state. Due to stoichiometry, the flux density of the reagents to the surface is  $j_1^{(s)} = j_2^{(s)} = -j_3^{(s)} = R$  or:

$$\kappa_1 \left( c_1 - c_1^{(s)} \right) = \kappa_2 \left( c_2 - c_2^{(s)} \right) = \kappa_3 \left( c_3^{(s)} - c_3 \right) = R. \quad (3)$$

The «microphysics» of the model is contained in this equation. In the present communication we assume the reaction to be fast, i.e. the external mass transfer in the gaseous phase to be rate-limiting, see [4, 5] and [6]. This means that the ratio of the mass transfer coefficients  $\kappa$  to surface reaction rate constant  $k$  is large  $\kappa/k \ll 1$  (since concentrations  $c_i$  are measured in dimensionless units,  $\kappa$  and  $k$  for the surface reaction are measured in the same units).

Our goal at this stage is to elaborate macroscopic equations to describe dynamics of concentrations at large scales. Therefore, we need to average out small scale phenomena at the single particle scale, but to take into account the mean effect of heterogeneous reaction to large scale dynamics. Thus, we need to introduce mean variables, averaged over an ensemble of particles. At this point we introduce the concept of *local concentration*. The local concentrations  $\bar{c}_i$  of species result from averaging of surface concentration  $c_i^{(s)}$  over all condensed phase particles of the same size in a physically small volume, positioned at a point with coordinates  $(x, y, z)$ , at the time  $t$ , that still contains a big number of aerosol particles. A size of this volume is supposed to be smaller than the typical scale of bulk gradients (cloud scale), but much larger than the droplet size. Thus, for a macroscopically nonuniform system, the local concentrations  $\bar{c}_i(t, x, y, z)$  are macroscopic variables, depending on macroscopic time and on large scale coordinates. We consider here an ensemble of identical particles,



that is monodisperse aerosols. In this case, the averaging procedure is simplified and one can associate the local concentrations  $\tilde{c}_i$  with mean values of surface concentrations  $c_i^{(s)}$ . That allows the next step – to average out surface concentrations in the mass action law (3) and to arrive at equations for macroscopic variables  $c_i$  and  $\tilde{c}_i$  only:

$$\kappa_1 (c_1 - \tilde{c}_1) = \kappa_2 (c_2 - \tilde{c}_2) = \kappa_3 (\tilde{c}_3 - c_3) = k \left( \tilde{c}_1 \tilde{c}_2 - \frac{1}{K} \tilde{c}_3 \right). \quad (4)$$

Now we turn to the macrophysics of the problem. At large scales (a cloud scale) the dynamics of bulk concentrations  $c_i$  is governed by three mass-conservation equations that take the form of the advection-diffusion equations with the source/sink term  $\Phi_i$  in the right-hand side

$$\frac{\partial c_i}{\partial t} + \mathbf{U} \cdot \nabla c_i = D \nabla^2 c_i - \Phi_i, \quad i = 1, 2, 3, \quad (5)$$

where  $D$  is the dispersion coefficient and  $\mathbf{U} = \text{const}$  is the velocity of superficial uniform flow in the frame of reference attached to the sedimenting droplets. At the cloud scale, that is at the scale which is much larger than the size of a single droplet, dispersion is due to turbulent mixing, so  $D$  may be identified as the turbulent diffusion coefficient and  $\Phi_1, \Phi_2$  are sinks and  $\Phi_3$  is a source due to chemical reaction. The difference in scales allows us to treat the mesoscale (scale of a single particle) transport by introducing macroscopic distributed sink and source terms  $\Phi_i$  in (5), phenomenologically averaging out mesoscale phenomena such as local mass transfer to and from the droplet surfaces. Using  $c_i$  and  $\tilde{c}_i$  introduced above, we write the sink and source terms in the conventional way

$$\Phi_i = S \kappa_i (c_i - \tilde{c}_i), \quad i = 1, 2, 3, \quad (6)$$

where  $S$  is the reactive surface per unit volume.

For uniform overall flow the macroscopic transport is essentially one dimensional. Thus, bulk concentrations  $c_i(t, z)$  and the local concentrations  $\tilde{c}_i(t, z)$  depend on time and a single macroscopic coordinate  $z$ . This, particularly, is a reasonable approximation for sedimenting particles.

Substituting equations for the  $\Phi_i$  (6) into (5) and taking into account the effective one-dimensionality of the macroscopic fluxes one arrives at

$$\frac{\partial c_i}{\partial t} + \mathcal{U} \frac{\partial c_i}{\partial z} = D \frac{\partial^2 c_i}{\partial z^2} - S \kappa_i (c_i - \tilde{c}_i), \quad i = 1, 2, 3, \quad (7)$$

where  $\mathcal{U} = |\mathbf{U}|$  and  $z$  is a macroscopic coordinate in the direction of the uniform flow  $\mathbf{U}$ .

For further analysis it is convenient to put the equations in non-dimensional form. All concentrations are measured in mole fractions and are already non-dimensional. The characteristic time scale  $\tau$  for the local mass transfer is  $\tau = [S \kappa_2]^{-1}$ . The characteristic length of turbulent diffusion during the time  $\tau$  is  $l = \sqrt{D\tau} = \sqrt{D/S \kappa_2}$ . The intrinsic scale  $l$  appears in the problem due to distinction between the bulk and local concentrations. The dimensionless time and coordinate are  $t' = t/\tau$ ;  $x = z/l$  respectively. We define also the dimensionless parameters  $\eta = k/\kappa_2$ ;  $\nu_1 = \kappa_1/\kappa_2$ ;  $\nu_2 = 1$ ;  $\nu_3 = \kappa_3/\kappa_2$ ; and  $p = \mathcal{U}/D$ . The



latter combination looks like a Péclet number; however, it is not a usual Péclet number, because  $D$  is not a molecular, but eddy diffusivity and the corresponding lengthscale  $l$  is not a geometrical size, but the intrinsic length characterizing the heterogeneous reaction. Finally, in the non-dimensional form, the basic system of equations reads:

$$\frac{\partial c_1}{\partial t'} = \frac{\partial^2 c_1}{\partial x^2} - p \frac{\partial c_1}{\partial x} - \nu_1 (c_1 - \tilde{c}_1), \quad (8)$$

$$\frac{\partial c_2}{\partial t'} = \frac{\partial^2 c_2}{\partial x^2} - p \frac{\partial c_2}{\partial x} - (c_2 - \tilde{c}_2), \quad (9)$$

$$\frac{\partial c_3}{\partial t'} = \frac{\partial^2 c_3}{\partial x^2} - p \frac{\partial c_3}{\partial x} - \nu_3 (c_3 - \tilde{c}_3), \quad (10)$$

$$\nu_1 (c_1 - \tilde{c}_1) = (c_2 - \tilde{c}_2) = \nu_3 (\tilde{c}_3 - c_3) = \eta \left( \tilde{c}_1 \tilde{c}_2 - \frac{1}{K} \tilde{c}_3 \right). \quad (11)$$

This closed system (8)-(11) is strongly nonlinear due to the nonlinear coupling between the bulk and local concentrations introduced by the equation (11). The equations (8)-(11), with suitable initial and boundary conditions, are a differential algebraic system (DAE), with three partial differential equation (PDE) constraints and three nonlinear algebraic constraints. DAEs are notoriously stiff, requiring careful numerical integration schemes to avoid instability. The model in this form in the context of heterogeneous chemical reactors theory was introduced and analyzed in [15–19].

In present communication we consider a particular type of heterogeneous reaction of two gaseous reactants with two reaction products, one of them is gaseous and the other one is non-volatile. The latter product is soluble and accumulates in the droplets. It is reasonable to assume that the concentrations of the non-volatile product at the surface of the droplet and inside the droplet rapidly reach the thermodynamic equilibrium described, e.g., by Henry's law. When a non-volatile product of reaction accumulates within the droplet, the ratio of reverse to forward reaction rates is increased. Therefore, due to shift of thermodynamic equilibrium with respect to solubility, the forward reaction eventually stops. Instead of following a gradual change of the equilibrium, we introduce the assumption of a finite capacity of droplets, due to solubility limitations, which yields a physically similar effect. Supposing that a cloud of droplets has a finite capacity for the accumulated species per unit volume  $Q = (\text{number of molecules, stored in a droplet}) \times (\text{number of droplets per unit volume})$ , we assume quenching of the reaction when the actual amount of non-volatile product in the droplets reaches this value (see Fig. 1). Due to stoichiometry, the amount of non-volatile product is proportional to the consumed amount of each reactant. Mathematically, the finite solubility assumption results in the imposition of an additional integral condition:

$$N \int (c_2 - \tilde{c}_2) dt = Q \quad (12)$$

where the integral is taken over time to saturation and  $N$  is the number of molecules per unit volume in the atmosphere. Despite the «kinematic appearance» of this constraint, it originates from thermodynamic equilibrium.

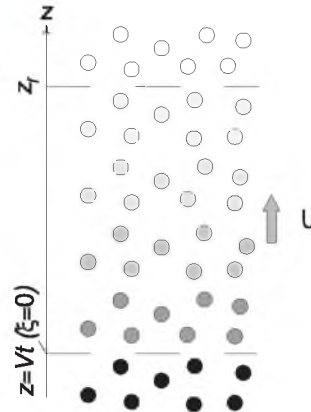


Fig. 1. Schematic presentation of the model: a uniform air flow with velocity  $U$  through a cloud of liquid particles. The downwards gradually increasing grayscale intensity corresponds to increasing content of non-volatile product.  $z_f$  is the far boundary of the reaction domain, where reaction starts;  $z = Vt$  is the position of saturation front, where the reaction ceases.

Additionally, assuming that the macroscopic scale  $L$  over which concentration changes is much less than the extent of the spatial domain, we analyze our model over an infinite domain.

**3. Propagating saturation front.** In this section we study the propagation of the reaction front through a cloud of aerosol droplets. When the air flow, containing premixed reactants  $A_1$  and  $A_2$ , enters the cloud, the reaction starts at the surface of the droplets. After a certain time, due to the finite capacity of droplets, the reaction ceases. Therefore, one can subdivide the whole domain into three regions: one where reaction has not yet started, the reaction zone, and the region where particles are already saturated with a non-volatile product and thus there is no reaction despite of the presence of both reactants in the surrounding air. Introducing the non-dimensional velocity  $v$  of the saturation front, we make a coordinate transformation to the frame moving with this front (see Fig. 1). The velocity  $V$  in Fig. 1 is related to non-dimensional velocity  $v$  by  $V = vl/\tau = v\sqrt{DS\kappa_2}$ . Defining the new coordinate by  $\xi = x - vt'$ , and looking for stationary solutions in the moving frame, equations (8)-(10) for the reaction zone take the form

$$\frac{\partial^2 c_i}{\partial \xi^2} - s \frac{\partial c_i}{\partial \xi} = \nu_i (c_i - \bar{c}_i) ; \quad i = 1, 2, 3, \tag{13}$$

where  $s = p - v$  and due to our normalization  $\nu_2 = 1$ . It is worth noticing that a stationary solution exists only in this reference frame; both in the frame coupled with the particles and in the frame moving with the overall flow, the process is essentially non-stationary.

In the domains without reaction the governing equations are

$$\frac{\partial^2 c_i}{\partial \xi^2} - s \frac{\partial c_i}{\partial \xi} = 0 ; \quad i = 1, 2, 3. \tag{14}$$

The above equations should be supplemented by boundary conditions. In the domain  $-\infty < \xi < 0$  the droplets are saturated by the non-volatile product. The spatial distribution



of concentrations is governed by the equations (14). The boundary conditions are

$$c_1|_{\xi \rightarrow -\infty} = c_1^\infty, \quad (15)$$

$$c_2|_{\xi \rightarrow -\infty} = c_2^\infty, \quad (16)$$

$$c_3|_{\xi \rightarrow -\infty} = 0. \quad (17)$$

In the reaction zone,  $0 < \xi < \xi^*$ , the concentrations are governed by the equations (11) and (13). The far boundary of this domain  $\xi^*$  corresponds to the point where the bulk concentrations of all components equal their local (surface) concentrations, that is, the difference  $\varphi = c_2 - \tilde{c}_2$  vanishes. For  $\xi^* < \xi < \infty$  the concentrations are again governed by equations (14). For  $\xi \rightarrow \infty$  all concentrations approach constant values. At  $\xi = 0$  and  $\xi = \xi^*$  the bulk concentrations and fluxes of all species are continuous.

In the present paper we consider an irreversible reaction, that is  $K$ , which is the ratio of reaction rate constants for the forward and reverse reactions tends to infinity. This means the limit  $1/K \rightarrow 0$  in the kinetic mass action law, last equality in (11) reads

$$\nu_3 (\tilde{c}_3 - c_3) = \eta \tilde{c}_1 \tilde{c}_2. \quad (18)$$

As already mentioned above, we assume reaction to be fast as compared to the external mass transfer in the gaseous phase [4], [5] and [6]. This means that  $\eta = k/\kappa_2$  tends to infinity  $\eta \rightarrow \infty$  and the quasi-stationary surface constraint (18) at leading order reads

$$\tilde{c}_1 \tilde{c}_2 = 0. \quad (19)$$

This equation means that for fast irreversible reaction in vicinity of the surface of a droplet at least one of the reactants is *completely* depleted. This does not mean, of course, the quenching of the reaction but just the immediate consumption of the reactant that is locally in deficit as it arrives at the surface of the droplet. For a single component such a situation at the surface of an individual particle is referred to as the «ideally absorbing condition» [4]. For the fast irreversible binary *homogeneous* reaction in a liquid layer a similar approach was developed by [24].

The non-linear analytic solution for large, but finite  $K$  and for large and finite  $\eta$  are also available [15] and [19]. The evaluation of corrections to this theory becomes essential for multiple reactions systems.

The equations governing the concentration of the product  $c_3$  are decoupled in the limit (19) from the equations governing concentrations of the reactants. Thus, the distribution of the product may be evaluated afterwards. In addition, the far boundary  $\xi^*$  of the reaction domain (i.e.  $z_f$  in laboratory frame, (see Fig. 1) is taken to infinity. Thus, only the reaction zone  $0 < \xi < \infty$  and the «saturated» region where the reaction is switched off  $-\infty < \xi < 0$  remain.

From the overall conservation of mass, see Appendix B, or alternatively, from smooth matching of solutions in reactive and non-reactive domains, it follows that  $s$  should be





positive. This implies that  $v < p$ , that is the saturation front moves slower than the flow. The general solutions of equations (14) in the non-reactive domain are

$$c_i = a_i \exp\{s \xi\} + c_i^\infty; \quad \xi < 0; \quad i = 1, 2. \quad (20)$$

where  $a_1$  and  $a_2$  are constants to be determined from the smooth matching of the solutions in adjacent domains.

Let us consider some global corollaries of (19). As mentioned above, the local concentration of at least one reactant is completely depleted, while the bulk concentrations  $c_1, c_2$  remain nonzero for any finite  $\xi$ ; the bulk concentration of the reagent which is in overall deficit (as compared to stoichiometric ratio) approaches zero in the limit  $\xi \rightarrow \infty$ . Obviously, either  $\tilde{c}_1$  or  $\tilde{c}_2$  may be zero everywhere, just because of an overall deficit of  $A_1$  or  $A_2$  respectively. However, the non-trivial possibility is the coexistence of domains of local depletion of different concentrations. This means that while in the vicinity of the surfaces of all particles in some macroscopic domain say, the reagent  $A_1$  is depleted, in the adjacent macroscopic domain in the vicinity of the surfaces of all particles are depleted is the reagent  $A_2$ . We show below that the necessary, but not sufficient condition for this to happen is the difference of the rates of local mass transfer. Generally, there are four possibilities:

1.  $A_1$  is in excess everywhere, that is due to the deficit of  $A_2$

$$\tilde{c}_2 = 0, \quad \tilde{c}_1(\xi) \neq 0, \quad 0 < \xi < \infty; \quad (21)$$

2.  $A_2$  is in excess everywhere, that is due to the deficit of  $A_1$

$$\tilde{c}_1 = 0, \quad \tilde{c}_2(\xi) \neq 0, \quad 0 < \xi < \infty; \quad (22)$$

3. Both reactants are completely depleted due to the reaction. Suppose, that the reactant  $A_1$  is more depleted near the origin ( $\xi = 0$ ), that is the local (in the vicinity of the particle surface) concentration  $\tilde{c}_1$  equals to zero. The reactant  $A_2$  is more depleted far away from the origin; in that domain the local concentration  $\tilde{c}_2$  in the vicinity of the particle surface is zero. The self-consistency of these assumptions will be verified later. There must be a point  $\xi = X$ , such that

$$\tilde{c}_1 = 0, \quad \tilde{c}_2(\xi) \neq 0, \quad 0 < \xi < X, \quad (23)$$

$$\tilde{c}_1(\xi) \neq 0, \quad \tilde{c}_2 = 0, \quad X < \xi < \infty; \quad (24)$$

4. Again both reactants are essentially depleted, but now the reactant  $A_2$  is more depleted near the origin ( $\xi = 0$ ). For this case

$$\tilde{c}_1(\xi) \neq 0, \quad \tilde{c}_2 = 0, \quad 0 < \xi < X, \quad (25)$$



$$\tilde{c}_1 = 0, \quad \tilde{c}_2(\xi) \neq 0, \quad X < \xi < \infty. \quad (26)$$

Of course, only two of these possibilities are physically different, therefore we consider below only cases 1 and 3. We would like to note here that the non-linear basic system degenerates in this limit to piecewise-linear system in adjacent spatial domains in cases 3 and 4. Thus, the problem remains non-linear due to the matching of the solutions in the adjacent domains. The fully nonlinear analysis by [15], [19] reveals the piecewise solution to be the correct leading order approximation in both small parameters proportional to  $1/K$  and  $1/\eta$ .

The cases 1 and 2 are simpler. The conditions (21) and (22), respectively, linearize the system. For the first case, for  $\tilde{c}_2 = 0$ ,  $\tilde{c}_1 \neq 0$ ,  $0 < \xi < \infty$  equations (13) for  $i = 1, 2$  read

$$\frac{\partial^2 \varphi}{\partial \xi^2} - s \frac{\partial \varphi}{\partial \xi} - \varphi = 0, \quad (27)$$

$$\frac{\partial^2 c_1}{\partial \xi^2} - s \frac{\partial c_1}{\partial \xi} = \varphi. \quad (28)$$

where for this particular case  $\varphi = c_2$ .

The solutions to (27) and (28), are exponentially decaying. Performing the smooth matching at  $\xi = 0$  for the solutions (20) and solutions of the system (27)-(28), we obtain for  $c_1$  and  $c_2$  finally

$$c_1 = c_1^\infty - \frac{\beta c_2^\infty}{\beta + s} \exp\{s \xi\}, \quad \xi < 0; \quad (29)$$

$$c_2 = c_2^\infty - \frac{\beta c_2^\infty}{\beta + s} \exp\{s \xi\}, \quad \xi < 0; \quad (30)$$

$$c_1 = \frac{s c_2^\infty}{\beta + s} \exp\{-\beta \xi\} + c_1^\infty - c_2^\infty, \quad \xi > 0, \quad (31)$$

$$c_2 = c_2^\infty \frac{s}{\beta + s} \exp\{-\beta \xi\}, \quad \xi > 0, \quad (32)$$

where  $\beta = \sqrt{\left(\frac{s}{2}\right)^2 + 1} - \frac{s}{2}$ .

The above solutions exist for arbitrary positive  $s = p - v$ . However, the actual value of non-dimensional velocity of the saturation front  $v$  is determined by the finite capacity assumption (see Section 2). Let us consider droplets at the (macroscopic) point  $x = 0$ , where  $x$  is a coordinate in the frame of reference immobile with respect to droplets. The reaction starts at time  $t'_{\text{start}} = -\infty$  and is turned off when the saturation front  $\xi = 0 - vt' = 0$  arrives at this point, that is  $t'_{\text{fin}} = 0$ . Taking  $t'_{\text{start}}$  and  $t'_{\text{fin}}$  as integration limits in the equation (12) one gets

$$N \int_{-\infty}^0 \varphi(-v\tau') d\tau' = Q. \quad (33)$$



Changing the integration variable  $\zeta = -v\tau'$  in (33) one obtains  $vQ/N = \int_0^\infty \varphi(\zeta)d\zeta$ . The integral may be evaluated either directly, using solution (32), or from the conservation of mass by integration of the equation (13) and (14) (see the Appendix B). This finally yields

$$v = \frac{p}{1 + \bar{Q}} ; \quad s = \frac{p}{1 + \bar{Q}^{-1}} , \quad (34)$$

where dimensionless  $\bar{Q} = Q/Nc_2^\infty$ . If the capacity of the droplets is large enough  $\bar{Q} \gg 1$ , then from eq. (34) it follows that  $s \approx p$ ; however the velocity of the saturation front  $v$  is necessarily smaller.

To determine the range of parameters corresponding to the present case  $\tilde{c}_1 \neq 0$  one has to calculate  $\tilde{c}_1$  for  $\xi > 0$  using the solution (32) and eq. (11):

$$\tilde{c}_1 = sc_2^\infty \frac{1}{\beta + s} \left( 1 - \frac{1}{\nu_1} \right) \exp \{ -\beta\xi \} + c_1^\infty - c_2^\infty , \quad (35)$$

If  $\nu_1 > 1$  then  $\tilde{c}_1$  decreases with  $\xi$  and

$$\min \{ \tilde{c}_1 \} = c_1^\infty - c_2^\infty . \quad (36)$$

If  $\nu_1 < 1$  then  $\tilde{c}_1$  increases with  $\xi$  and

$$\min \{ \tilde{c}_1 \} = c_1^\infty - c_2^\infty \frac{\nu_1\beta + s}{\nu_1(\beta + s)} . \quad (37)$$

If  $\min \{ \tilde{c}_1 \}$  becomes negative, the assumption of preferential depletion of the reactant  $A_2$  in the whole domain (21), is violated either in the vicinity of  $\xi = 0$  or at infinity, so either case 3 or case 4 must be considered. If such «exchange of depletion», or «crossover», takes place for  $\xi > 0$ , one has two subdomains. In each subdomain the method of solution is essentially the same; however the matching of solutions in both subdomains at the point  $\xi = X$ , is needed, see (23)-(26).

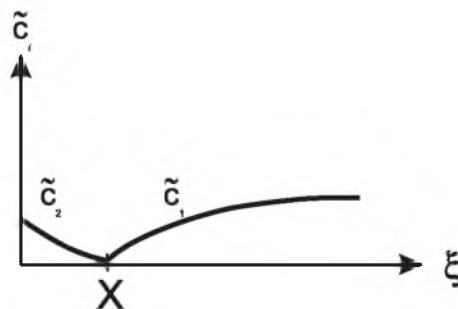


Fig. 2. Schematic presentation of the local concentrations  $\tilde{c}_1$  and  $\tilde{c}_2$  as functions of the coordinate  $\xi$  in the moving frame for the case 3.



For the third case, (see Fig. 2) in the subdomain  $0 < \xi < X$ , where  $\bar{c}_1 = 0$ ,  $\bar{c}_2(\xi) \neq 0$ , one obtains

$$\frac{\partial^2 c_1}{\partial \xi^2} - s \frac{\partial c_1}{\partial \xi} - \nu_1 c_1 = 0, \quad (38)$$

$$\frac{\partial^2 c_2}{\partial \xi^2} - s \frac{\partial c_2}{\partial \xi} = \nu_1 c_1. \quad (39)$$

Solutions of these equations should be matched with (20) at  $\xi = 0$ .

In the subdomain  $X < \xi < \infty$  concentrations  $c_1$  and  $c_2$  are governed by the equations (27)-(28). Their solutions should be matched with the solutions of (38) and (39) at the boundary  $\xi = X$ . Then  $X$  is determined by the transcendental equation:

$$\frac{\alpha_1^2(1 + \alpha_2\beta)e^{\alpha_2 X} + \alpha_2^2(\alpha_1\beta - 1)e^{-\alpha_1 X}}{s(1 - \nu_1)(\alpha_1 + \alpha_2)} = \frac{\sigma}{\sigma - 1}, \quad (40)$$

where  $\sigma = c_1^\infty / c_2^\infty$ ,  $\alpha_1 = \sqrt{\left(\frac{s}{2}\right)^2 + \nu_1 + \frac{s}{2}}$  and  $\alpha_2 = \sqrt{\left(\frac{s}{2}\right)^2 + \nu_1 - \frac{s}{2}}$ . Thus, four conditions of smooth matching of the solutions at  $\xi = X$  result in a single transcendental equation that we analyze numerically below. The complete solution to the problem (27), (28), (38), (39) and (40) with corresponding boundary conditions can now be easily written down; being cumbersome they are given in the Appendix C). This solution depends parametrically on  $X$  which is a root of the equation (40). For the existence of this case the parameter  $\sigma$  should satisfy

$$1 < \sigma < 1 + \frac{s\beta(1 - \nu_1)}{\nu_1}, \quad (41)$$

that is, the «faster» reagent should have lower value of the initial concentration, but this difference should not be too large.

**4. Discussion and conclusions.** The solution obtained describes propagation of a heterogeneous chemical reaction through a cloud of liquid droplets. The saturation front, that is the boundary of the region where the particles are already saturated, moves with a constant velocity  $v$  which is expressed through the uniform flow velocity  $p$  by equation (34) for cases 1 and 3 and equation (57) for cases 2 and 4. It also depends on the dimensionless capacity  $\bar{Q}$  of the droplets. The solutions are stationary in a frame moving with the velocity  $v$  with respect to the cloud of droplets;  $v$  is necessarily smaller than  $p$ .

The steady lag of the saturation front relative to overall flow translates into a steady widening of macroscopic reaction domain. Qualitatively this continuously decreases the observed local intensity of reaction. Consequently, the observed mean rate for a heterogeneous reaction producing a product stored in the particles, will be lower for an descending cloud of particles, than for a quiescent cloud. Thus we hypothesize that the observed confinement of the reactions of this type in polar stratospheric clouds to a definite altitude, which is rightly attributed to temperature, pressure and radiative conditions, may have an additional, purely dynamic cause.

The point  $\xi = X$ , which is also moving with the velocity  $v$  with respect to droplets, separates the region where the local concentration  $\bar{c}_1$  is depleted from the region where  $\bar{c}_2$  is



depleted. In the approximation of irreversible reaction ( $K \rightarrow \infty$ ) both local concentrations  $\tilde{c}_1$  and  $\tilde{c}_2$  vanish at the  $X$ -point. We would like to emphasize that the position of this “switch-point”  $X$  is determined in a self-consistent way.  $X$  as solution of the equation (40) depends on  $\sigma$ ,  $s$  and  $\nu_1$ . In Fig. 3 we present  $X$  as function of  $\sigma$  and  $s$  for fixed value of  $\nu_1$ .

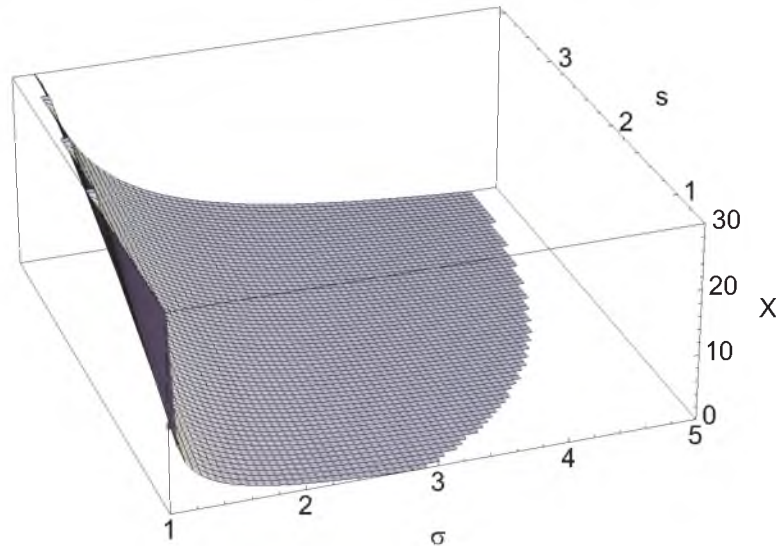


Fig. 3. Position of switch point  $X$  as function of concentration ratio  $\sigma$  and flow velocity  $s$  in moving frame for  $\nu_1 = 0.2$ .

It is easily seen from (41), that  $\nu_1 < 1$  is the necessary though not sufficient condition for the existence of the *switch-point*  $X$ . Since  $\nu_1 = \kappa_1/\kappa_2$  is the ratio of mass-transfer coefficients  $\nu_1 \neq 1$  is a manifestation of the asymmetry in mesoscopic mass-transfer. An aerosol particle in the flow is surrounded by a boundary layer. Even though the boundary layer can be turbulent, in the near field of the surface there is always a laminar boundary layer in which the transport of the molecules is due to molecular diffusion which is different for different species, that is  $\nu_1 \neq 1$ .  $X$  as function of  $\nu_1$  at fixed values of  $\sigma$  and  $s$  is presented in Fig. 4.

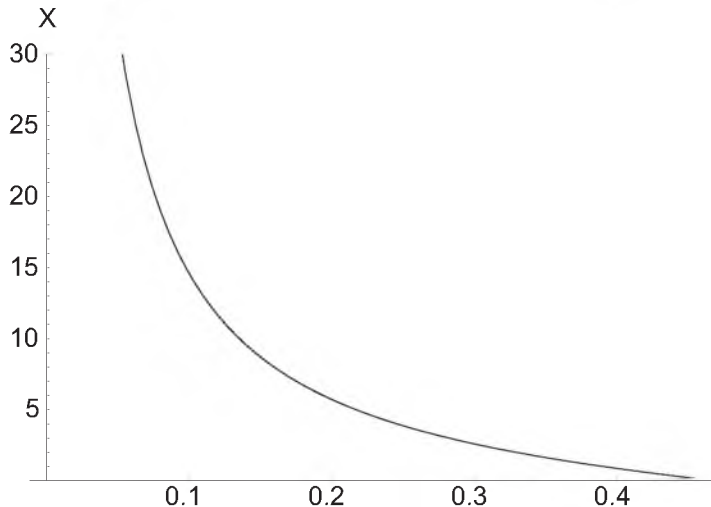


Fig. 4. Position of switch point  $X$  as function of the ratio of mass transfer coefficients  $\nu_1$  at fixed  $\sigma = 2.0$  and  $s = 2.5$ .



The uptake of reactants and, respectively, the generation of the product are space/time dependent and fundamentally controlled by the existence of a switch point  $X$ . At the switch-point, the local excess of reactant  $A_2$  is replaced by the local excess of reactant  $A_1$ . For the case considered, the ratio of the initial concentrations  $c_1^\infty/c_2^\infty$  of the reactants  $A_1$  and  $A_2$  exceeds the stoichiometric ratio. Therefore one is tempted to consider the reaction in the whole domain as quasi-first order with respect to  $A_2$ . This would be equivalent to a traditional model, which neglects the change of the local concentration due to the «switch». However, the change of the regime has a dramatic effect on the distribution of the reaction product. Indeed, let us compare the modeling of the reaction with and without the switch point; the latter corresponds to traditional modeling.

The generation of the product (uptake of the reactants) is proportional to the integrals of supersaturation  $\varphi$  over reaction domain (see eq. (12) and (54)). To estimate the error in uptake of the reactants (or the yield of the reaction products) in the domain  $[0, \xi_m]$ , which is introduced by ignoring the switch, that is not considering the evolution of the local concentrations, it is expedient to consider the relative error  $E_{\text{rel}}$

$$E_{\text{rel}}(\xi_m) = \left( \int_0^{\xi_m} \varphi^* d\xi - \int_0^{\xi_m} \varphi d\xi \right) / \int_0^{\xi_m} \varphi d\xi, \quad (42)$$

where  $\varphi^*$  is evaluated ignoring the existence of the switch, assuming the local excess of the reactant  $A_1$  in the whole domain. The relative error  $E_{\text{rel}}$  as a function of  $\xi_m$  is shown in the Fig. 5.

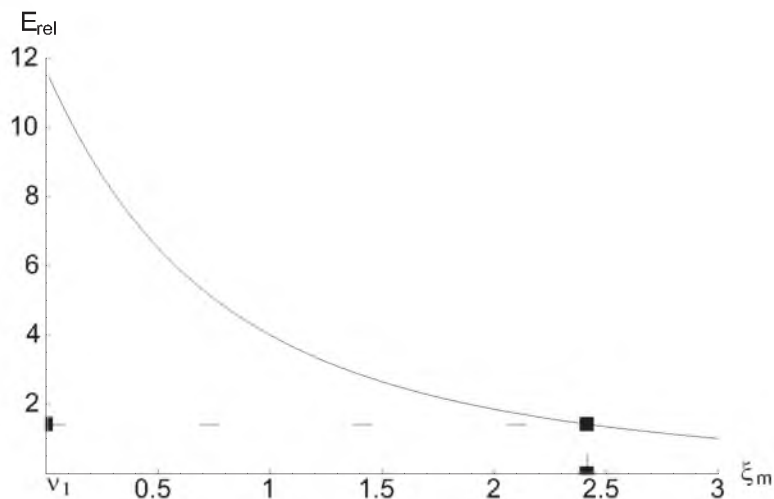


Fig. 5. The relative error  $E_{\text{rel}}$  as function of  $\xi_m$  at fixed values of  $\sigma = 2.0$ ,  $s = 2.0$  and  $\nu_1 = 0.2$ . The position  $\xi_m = 1/\beta = 2.41$  and the corresponding value  $E_{\text{rel}}(2.41) = 1.42$  are indicated.

If we ignore the switch and admit quasi-first order decay (40), the characteristic decay length of  $\varphi$  is  $1/\beta$ . So to estimate the lower bound of the error, we take  $\xi_m = 1/\beta$  (see Fig. 5). For this special position the error is about 40%; however, for  $\xi_m = 1$  the error increases



tenfold up to 400%. That is, even for the simple case of a single-reaction, neglecting local concentration changes may result in a substantial error in the uptake of reactants.

The dependence of  $E_{\text{rel}}(\beta^{-1})$  as a function of parameters  $\sigma$  and  $s$  is presented in Fig. 6. This dependence clearly resembles the function  $X(\sigma, s)$ , presented in the Fig. 3. This is a manifestation of the importance of the crossover or switch point.

To estimate the value of  $s = p/(1 + \bar{Q}^{-1})$ , where  $\bar{Q}$  is a relative capacity of the droplets with respect to nonvolatile reaction product, we notice that the effect of saturation of the droplets on the overall distribution of concentration is substantial only if  $\bar{Q} \gg 1$ . Thus, as an estimate of  $s$  one can take  $s \approx p$ , where  $p$  is the non-dimensional relative velocity of droplets with respect to ambient air. Considering an ensemble of droplets sedimenting in the air one can estimate the velocity using the Stokes formula (see e.g. [4]).

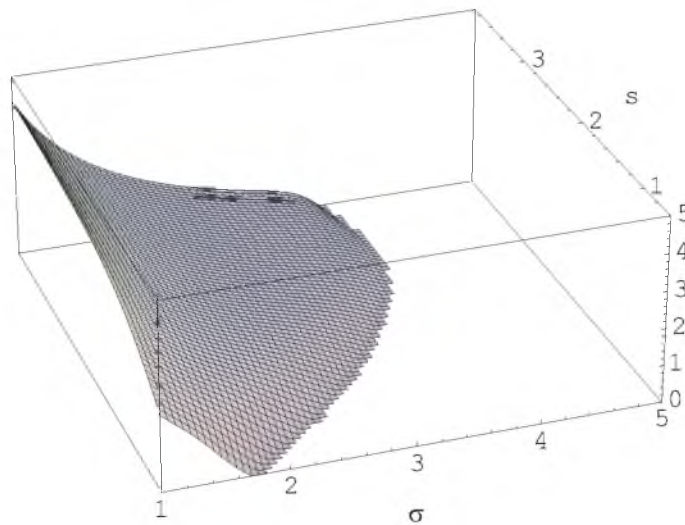


Fig. 6. Relative error  $E_{\text{rel}}(1/\beta)$  as function of the  $\sigma$  and  $s$  at fixed value of  $\nu_1 = 0.2$ .

Now we give some estimates using known atmospheric data, for the example of the heterogeneous reaction of chlorine nitrate with hydrochloric acid at the surface of stratospheric aerosol particles. Assuming a free molecular regime for mass transfer (see e.g. [6]), the mass transfer coefficients  $\kappa_1$  and  $\kappa_2$  may be evaluated using the formula  $\kappa = \alpha \bar{v}/4$ , where  $\alpha$  is the mass accommodation coefficient and  $\bar{v} = \sqrt{8kT/\pi m_0}$ . Here  $k$  is Boltzmann's constant, and  $m_0$  is the mass of a molecule of species in question. Taking the value of  $T = 222$  K at the altitude 25 km (see Appendix B in [8]) and assuming the values of mass accommodation coefficients of HCl and ClONO<sub>2</sub> as 0.1 and 0.03 respectively one arrives at the values of  $\kappa_1 = 1.68$  and  $\kappa_2 = 9.14$  m/s. The estimate of sedimentation velocity at the same altitude using the Stokes formula (see e.g. [4]) yields the value of order  $10^{-4}$  m/s. To estimate the approximate value of  $s \approx p$ , where the non-dimensional velocity  $p$  is defined above as  $p = U/\sqrt{S\kappa_2 D}$ , we use the surface to volume ratio  $S = 10^{-6}$  m<sup>2</sup>/m<sup>3</sup> [13] and  $D \approx 10^{-3}$  m<sup>2</sup>/s. Dole et al. [25] give the estimate of turbulent diffusion in the stratosphere as  $D$  less than  $10^{-2}$  m<sup>2</sup>/s based on the measurement by atmospheric radar PROUST. Then  $s$  is of the order of one; the ratio  $\nu_1 \approx 0.2$ . We used values of this order of magnitude in the examples exhibited in Figs. 3-6.



To avoid misunderstanding we would like to point out that the above numerical estimates, based on particular atmospheric data, reveal the importance of the exchange of local depletion and estimate a possible error introduced by ignoring the detailed evolution of the local concentrations in space/time evolving systems.

On the other hand, the spreading of the saturation front, and as a consequence «smearing» of reaction over a wider spatial domain in a descending layer of particles, is quite a «coarse» effect for a mass-transfer-limited reaction of the above mentioned type, based on conservation of mass and on the interplay of overall mass transport and the sinks/sources due to the presence of particles, weakly dependent on the details of kinetics and values of the reaction rate constant.

We have considered above an ensemble of identical particles. Being reasonable first approximation this is still a simplification of reality. For identical particles there is a single local concentration of the species for all particles at the same physical point, see Section 2. For  $N_s$  discrete size classes the averaging results in  $N_s$  different variables, that is a local concentration,  $\bar{c}_i^n$ ,  $n = 1, 2, \dots, N_s$  for each size class. This results in a drastic increase in the number of governing equations. All parameters of local mass transfer and reaction kinetics, introduced in this communication for an ensemble of identical particles, will also differ for different size classes. Still, the same approach may be applied; however for polydisperse aerosols the mathematics becomes much more involved. The effects of particle size distribution will be subject of a special communication.

In summary, a model, describing fast heterogeneous chemical reaction and mass transfer in a one-dimensional overall flow has been developed. If the basic system of equations is supplemented by the finite capacity assumption reflecting the finite storage ability with respect to a non-volatile product, a travelling-wave regime exists. In this regime, the width of the reaction domain tends to increase. This system may be extended in a rather straightforward way to include multicomponent, multiple reactions, several kinds of particles and different size classes. As shown in [15], essentially the same approach may be used to analyze a «batch reactor» – in the context of aerosol systems, this constitutes a well mixed «parcel» of air or laboratory experiments in a chamber. For a reversible reaction finite  $K$  should be considered. To solve the problem for small, but finite  $K$  we have to use the modified Thiele moduli (mTm) approach see [16–18] and [19]. The interplay of local and global mass-transfer is taken into account in a self-consistent way. As a consequence, even if one of the reactants initially is in local excess, crossover may happen due to asymmetry in mass transfer coefficients. This may result in significant corrections to the uptake of reactants and the spatial-temporal distribution of the products.

**Appendix A.** We assume the following mechanism for heterogeneous reaction



where only the second step represents chemical kinetics:  $k^+$  and  $k^-$  are rate coefficients for the forward and reverse reactions, respectively, on the surface. If  $A_1$  is identified with





HCl,  $A_2$  with ClONO<sub>2</sub>,  $A_3$  with Cl<sub>2</sub>, and  $A_4$  with HNO<sub>3</sub>, the model (43)-(45) applies under reasonable assumptions for the reaction of chlorine activation, considered in the present paper as an example. The kinetic expression for this mechanism will be derived below, but first we introduce the following notations for the concentrations at the surfaces of the particles  $c_i^{(s)}$  and their relative surface coverages  $s_i$

$A_1$	$c_1^{(s)}$	$s_1$
$A_2$	$c_2^{(s)}$	-
$A_3$	$c_3^{(s)}$	-
$A_4$	-	$s_4$

If for  $A_1$  the Langmuir kinetics is assumed, the mass balance on the surface is given by equations

$$\frac{ds_1}{dt} = k_1 c_1^{(s)} (1 - s_1 - s_4) - k'_1 s_1 - k^+ s_1 c_2^{(s)} + k^- c_3^{(s)} s_4, \quad (46)$$

$$\frac{ds_4}{dt} = k^+ s_1 c_2^{(s)} - k^- c_3^{(s)} s_4 - b \left[ s_4 - (s_4)_{\text{equil}} \right], \quad (47)$$

where  $k_i$  and  $k'_i$  are adsorption and desorption rate constants, respectively;  $b$  is the dissolution rate constant, and  $(s_4)_{\text{equil}}$  is the equilibrium value of  $s_4$ , determined by the instantaneous content of  $A_4$  inside the droplet (the diffusion of the non-volatile product  $A_4$  inside the small droplet is considered as fast and not rate-limiting).

Making the common assumption of a pseudo - stationary state at the surface, we obtain

$$c_1^{(s)} (1 - s_1 - s_4) - a_1 s_1 - \frac{k^+}{k_1} s_1 c_2^{(s)} + \frac{k^-}{k_1} c_3^{(s)} s_4 = 0, \quad (48)$$

$$\frac{k^+}{k_1} s_1 c_2^{(s)} - \frac{k^-}{k_1} c_3^{(s)} s_4 - a_2 \left[ s_4 - (s_4)_{\text{equil}} \right] = 0, \quad (49)$$

where  $a_1 = k'_1/k_1$ ;  $a_2 = b/k_1$ . Solution of this system for  $s_1$ ,  $s_4$ , though elementary, yields quite cumbersome expressions. However, the exact solutions are not needed within the scope of the present communication. Indeed, our consideration is restricted to the case when the adsorption/desorption and dissolution kinetics are fast in comparison to all other processes; that is  $k^+/k_1 \ll 1$ ,  $k^-/k_1 \ll 1$ , while  $a_1$ ,  $a_2$  are neither too large, nor too small. It follows from (49), that  $s_4 \simeq (s_4)_{\text{equil}}$ . According to our finite capacity assumption, we do not treat the gradual increase of  $(s_4)_{\text{equil}}$  caused by increased content of  $A_4$  in the droplet. Instead, we assume it to be constant and small; thus the reaction is switched off when the limiting content of  $A_4$  in the droplet is reached.

For  $s_1$  the same assumptions yield

$$s_1 = \frac{c_1^{(s)}/a_1}{1 + c_1^{(s)}/a_1}. \quad (50)$$

Then the expression for the reaction rate  $R$  is :

$$R = \frac{k^+}{a_1} \cdot \frac{c_1^{(s)} c_2^{(s)}}{1 + c_1^{(s)}/a_1} - k^- (s_4)_{\text{equil}} c_3^{(s)}; \quad (51)$$



or, introducing rate constant  $k = k^+ / a_1$  and effective equilibrium constant

$$K = k^+ / \left[ a_1 k^- (s_4)_{\text{equil}} \right]$$

for the surface reaction,

$$R = k \left( \frac{c_1^{(s)} c_2^{(s)}}{1 + c_1^{(s)} / a_1} - \frac{c_3^{(s)}}{K} \right). \quad (52)$$

This equation still differs from (2) of Section 2 by the Langmuir multiplier,  $1 + c_1^{(s)} / a_1$ , which is close to unity only for the relatively low coverage of the surface. This multiplier is taken into account in [19] and shown to be of possible importance for reversible reaction. In the present paper, for large  $k$  and  $K \rightarrow \infty$ , that is for fast irreversible reaction, both (52) and (40) result in the same limiting form,  $c_1^{(s)} c_2^{(s)} \rightarrow 0$ . See the corresponding equation (19) for the local concentrations.

**Appendix B.** Let us integrate equation (14) over domain  $-\infty < \xi < 0$ , and equation (13) over domain  $0 < \xi < \infty$ :

$$\left. \frac{\partial c_2}{\partial \xi} \right|_{-\infty}^0 - s c_2|_{-\infty}^0 = 0, \quad (53)$$

$$\left. \frac{\partial c_2}{\partial \xi} \right|_0^\infty - s c_2|_0^\infty - \int_0^\infty \varphi(\xi) d\xi = 0. \quad (54)$$

Both  $c_2$  and  $\partial c_2 / \partial \xi$  are continuous at  $\xi = 0$ ; therefore

$$s c_2|_{-\infty}^\infty = - \int_0^\infty \varphi(\xi) d\xi, \quad (55)$$

or

$$[c_2^\infty - c_2|_{+\infty}] s = \frac{n}{N} v Q. \quad (56)$$

For the cases 1 and 3  $c_2|_{+\infty} = 0$ ; this immediately yields the result equation (34). Exactly the same procedure, but applied to equations (14) and (13) yields for the cases 2 and 4:

$$v = \frac{p}{1 + Q/\sigma}. \quad (57)$$

**Appendix C.** Here the full solution for the third case, see (23)-(24) and (38)-(41), is given. For  $0 < \xi < X$

$$c_1 = \frac{1}{\alpha_1 \exp(\alpha_2 X) + \alpha_2 \exp(-\alpha_1 X)} \left[ \left[ \alpha_1 \frac{c_1^\infty - c_2^\infty}{1 - \nu_1} \exp(\alpha_2 X) - s c_1^\infty \right] \times \right. \\ \left. \times \exp(-\alpha_1 (X - \xi)) + \left[ \alpha_2 \frac{c_1^\infty - c_2^\infty}{1 - \nu_1} \exp(-\alpha_1 X) + s c_1^\infty \right] \exp(\alpha_2 (X - \xi)) \right], \quad (58)$$



$$c_2 = c_1 - c_1^\infty + c_2^\infty, \tag{59}$$

$$\tilde{c}_1 = 0; \quad \tilde{c}_2 = (1 - \nu_1) c_1 - c_1^\infty + c_2^\infty. \tag{60}$$

For  $X < \xi < \infty$

$$c_1 = \nu_1 \frac{c_1^\infty - c_2^\infty}{1 - \nu_1} \exp(-\beta(\xi - X)) + c_1^\infty - c_2^\infty, \tag{61}$$

$$c_2 = \nu_1 \frac{c_1^\infty - c_2^\infty}{1 - \nu_1} \exp(-\beta(\xi - X)), \tag{62}$$

$$\tilde{c}_1 = c_1^\infty - c_2^\infty - (c_1^\infty - c_2^\infty) \exp(-\beta(\xi - X)), \quad \tilde{c}_2 = 0, \tag{63}$$

Both bulk concentrations are decreasing for  $\xi \rightarrow \infty$ ; while the concentration of the reagent  $A_2$  which is in deficit with respect to stoichiometric ratio approaches zero, the concentration of the reagent  $A_1$  approaches  $c_1^\infty - c_2^\infty$ . However, while the local concentration  $\tilde{c}_2$  is decreasing from some finite value at  $\xi = 0$  to zero at  $\xi = X$  and remains zero for larger  $\xi$ , the local concentration  $\tilde{c}_1$  increases from zero at  $\xi = X$  to  $c_1^\infty - c_2^\infty$  for  $\xi \rightarrow \infty$ , see Fig 1. The simple relation between the bulk concentrations, (59), (61), and (62) is a direct consequence of the equal dispersion coefficients for all species in the equations for the macroscopic mass transport, eq.(7). However, the method of solution outlined in the present communication does not use this fact, so it is valid for the case of different dispersion coefficients as well, when there is no such simple connection. The above solutions depend parametrically on  $X$ , which is a root of the equation (40). For the present case to exist the ratio  $\sigma$  of the initial concentrations should belong to the interval  $[1, 1 + s\beta(1 - \nu_1)/\nu_1]$ , see (41). One can see from (40), that  $X$  approaches zero when  $\sigma$  approaches the upper limit. This means that the solutions (61)-(63), representing the local deficit of  $A_2$ , become valid starting from  $\xi = 0$ , that is the Case 1 – for sufficiently large excess of initial concentration  $A_1$  is both in global and (despite slower mass transfer) local excess over whole reactive domain. On the other hand, if  $\sigma$  approaches the lower limit,  $X$  tends to infinity, that is the domain where solutions (58)- (60) are valid spreads over all  $\xi$ . This means, in its turn, that we approach the Case 2, when  $A_1$  is in global and local deficit in the whole reactive domain.

The above consideration presumes  $\nu_1 < 1$ . Of course, for  $\nu_1 > 1$  the switch is also possible; however, than it should be  $\sigma < 1$ , but again, not too small (Case 4). It is worth noticing, that each of the (physically equivalent) Cases 1 and 2 is possible both for  $\nu_1 < 1$  and  $\nu_1 > 1$ , see eqs. (36),(37) for the Case 1. This corresponds to a single non-zero local concentration either increasing, or decreasing with  $\xi$  in the whole reactive domain; of course, the difference between the corresponding bulk and local concentrations, which is the driving force for the process, always decreases with  $\xi$ . Such non-trivial and non-monotonic parametric dependence is a manifestation of the strongly nonlinear character of the problem considered.

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### References

1. Warneck P. Fundamentals // in: Global aspects of atmospheric chemistry. Topics in physical chemistry / Vol. 6, ed. by Deutsche Bunsen-Gesellschaft für Physikalische Chemie e.V., R. Zellner, guest editor / Springer: Darmstadt, New York, 1999. – P.1-20.
2. Calvert J.G. (Ed.): SO<sub>2</sub>, NO, NO<sub>2</sub> Oxidation Mechanisms: Atmospheric Considerations / Butterworth: Boston, 1984.
3. Zellner R. Chemistry of Stratosphere // in: Global aspects of atmospheric chemistry. Topics in physical chemistry, Vol. 6, ed. by Deutsche Bunsen-Gesellschaft für Physikalische Chemie e.V., R. Zellner guest editor / Springer: Darmstadt, New York, 1999. –P.181-254.
4. Schwartz S.E. Mass transport considerations pertinent to to aqueous phase reactions of gases in liquid-water clouds // in: Chemistry of multiphase atmospheric systems, Ed. W.Jaeschke, NATO ASI series. – Vol. G6, 1986.
5. Jacob D.J. Heterogeneous chemistry and tropospheric ozone // Atmospheric Environment. – 2000. – 34. – P.2131-2159.
6. Widmann J.F., Davies E.J. Mathematical models of the uptake of ClONO<sub>2</sub> and other gases by atmospheric aerosols // J. Aerosol Sci. – 1997. – 28(1). – P.87-106.
7. Seinfeld J.H. Atmospheric chemistry and physics of air pollution / John Wiley & Sons: N-Y., 1986.
8. Jacobson M.Z. Fundamentals of atmospheric modeling / Cambridge University Press, 1999.
9. Ravishankara A.R. Heterogeneous and multiphase chemistry in the Troposphere // Science. – 1997. – 276. – P.1058-1065.
10. Pilinis C., Seinfeld J.H., Seigneur C. Mathematical modeling of the dynamics of multicomponent atmospheric aerosols // Atmos. Environ. – 1987. – 21. – P.943-955.
11. Koo B., Gaydos T.M., Pandis S.N. Evaluation of the equilibrium, dynamic, and hybrid aerosol modeling approaches // Aerosol Science and Technology. – 2003. – 37. – P.53-64.
12. Meng Z., Seinfeld J.H. Time scales to achieve atmospheric gas-aerosol equilibrium for volatile species // Atmospheric Environment. – 1996. – 30. – P.2889-2900.
13. Tabazadeh A., Turco R. A model for heterogeneous chemical process on the surface of ice and nitric acid trihydrate particles // J. Geophys. Res. – 1993. – 98(D7). – P.12727-12740.
14. Hanson D.R., Ravishankara A.R., Solomon S. Heterogeneous reactions in sulfuric acid aerosols: A framework for model calculations // J. Geophys. Res. – 1994. – 99(D2). – P.3615-3629.
15. Mchedlov-Petrosyan P.O., Zimmerman W.B., Khomenko G. Fast binary reactions in a heterogeneous catalytic batch reactor // Chemical Engineering Science. – 2003. – 58(12). – P.2691-2703.
16. Mchedlov-Petrosyan P.O., Khomenko G., Zimmerman W.B. Nearly irreversible, fast heterogeneous reactions in premixed flow // Chemical Engineering Science. – 2003. – 58(13). – P.3005-3023.
17. Mchedlov-Petrosyan P.O., Khomenko G., Zimmerman W.B. Fast heterogeneous catalytic reactions in a CST reactor: perturbative approach // Kharkov University Bulletin, Chemical series. – 2001. – 7(30). – P.53-65.
18. Zimmerman W.B., Mchedlov-Petrosyan P.O., Khomenko G.A. Diffusion limited mixing and reaction in heterogeneous catalysis of initially segregated species // Chemie Symposium Series. – 1999. – 146. – P.317-324.
19. Zimmerman W.B., Mchedlov-Petrosyan P.O., Khomenko G.A. Nonequilibrium effects on fast binary reactions in a heterogeneous catalytic batch reactor // Chemical Engineering Science. – 2005. – 60. – P.3061-3076.
20. Deshpande K.B., Zimmerman W.B. Experimental study of mass transfer limited reaction. Part I: A novel approach to infer asymmetric mass transfer coefficients // Chemical Engineering Science. – 2005. – 60(11). – P.2879-2893.



21. Deshpande K.B., Zimmerman W.B. Experimental study of mass transfer limited reaction. Part II: Existence of crossover phenomenon // Chemical Engineering Science. – 2005. – 60;№15. – P.4147-4156.
22. Soo S.L. Fluid Dynamics of Multiphase Systems / Blaisdell Publ.: Massachusetts-Toronto-London, 1967.
23. Satterfield C.N. Mass transfer in heterogeneous catalysis / MIT Press: Cambridge, Mass., 1970.
24. Dankwerts P.V. Absorption by simultaneous diffusion and chemical reaction // Transactions of the Faraday Society. – 1950. – 46. – P.300-304.
25. Dole J., Wilson R., Dalaudier F., Sidi C. Energetics of small scale turbulence in the lower stratosphere from high resolution radar measurements // Annales Geophysicae. – 2001. – 19. – P.945-952.

### О РАСПРОСТРАНЕНИИ ФРОНТА НАСЫЩЕНИЯ ГЕТЕРОГЕННОЙ ХИМИЧЕСКОЙ РЕАКЦИИ В АЭРОЗОЛЬНОМ ОБЛАКЕ

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**Аннотация.** Облако аэрозольных частиц осаждается в воздухе, содержащем реагенты. Исходя из макроскопической модели химии и массопереноса, основанной на кинетической теории гетерогенных химических реакций, мы анализируем распространение химической реакции в облаке аэрозольных частиц. В этой работе мы рассматриваем бинарную реакцию с одним летучим и одним нелетучим продуктом, протекающую на поверхности аэрозольных частиц. Если принять во внимание конечную ёмкость капли по насыщению нелетучим продуктом реакции, замедление реакции в конце концов приводит к распространению фронта насыщения. Найдены пространственное распределение концентраций, их эволюция со временем и скорость фронта насыщения.

**Ключевые слова:** аэрозоль, капля, гетерогенная химическая реакция, массоперенос.