Chapter 4

A chemical kinetic model for reactive transformations of aerosol particles

Previous models of heterogeneous interactions have focused on reactive trace gas depletion in cloud or aerosol particles and droplets.[1,2,3] However, recent laboratory studies have demonstrated that reactive trace gas uptake can significantly transform the chemical composition of condensed phase species, as is evident from recent work on organic aerosols.[4,5] This model focuses on transformation rates within the particle itself. In limiting cases, the model leads to simple analytical expressions for the condensed phase species depletion as a function of aerosol/gas interaction time. The model takes into account gas phase diffusion, mass accommodation, bulk phase chemical reactions, surface reactions and particle phase reactant diffusion from the aerosol interior toward the surface. In this way, five limiting regimes of aerosol chemical kinetic processing are identified, quantified, and united to form a single comprehensive mathematical model of particle phase species kinetics. The presentation stresses the information to be gained from observing the size dependence of the particle phase decay rate. Indeed, decay rates exhibiting size dependence spanning particle radius, r^0 through r^{-2} are theoretically feasible, and rates going as r^0 and r^{-1} have been experimentally observed[1,4].

In addition, an appendix is provided in which existing characteristic times are summarized or new ones are derived for each of the five relevant regimes of chemical processing. Characteristic times can be quickly compared to both time-scales of observed changes in laboratory or field studies *and* apparent size dependence of reaction rates. Such time scales offer a reliable indicator of the fundamental processes most likely to govern the overall reaction rate. They also reveal what combinations of physico-chemical parameters will be obtained in studying the time dependence of that process. In this way they form a useful compliment to the resistor model described below. The method of characteristic times applied to cloud droplets was first described by Schwartz[6].

4.1 Modeling interactions between aerosols and reactive trace gases

An aerosol of known size and initial composition is exposed to a reactive trace gas for a known period of time, t. The experimentally observed quantity to be modeled here is the loss rate of particle phase species, as opposed to the disappearance of gas phase reactants, the focus of previous studies. We assume the chemical reaction between the trace gas X and particle phase species Y is irreversible; that is, $X + Y$ ® Z, where Z represents one or more product species. The method presented here can nonetheless be extended to more complicated chemical kinetic scenarios. In general, in the absence of convective mixing, the overall kinetic processing will depend on the chemical reaction rates as well as the mass transport of both particle and gas phase species. Many parts of the model presented here are taken from our recent paper on the same subject[7].

The conceptual strategy

Our goal is to mathematically describe a general physical system for which all of the relevant physics (in the form of partial differential equations) is known, but that cannot be represented by any known analytical solution. To our knowledge, even numerical solutions have not been developed over the full range of conditions considered here. However, the system is well described at various limits. In such limits, the partial differential equations reduce to forms that can be solved analytically by standard methods such as separation of variables or Fourier transforms. Our strategy is to construct a mathematical basis set from a collection of such physically limiting regimes, which we conceive as *resistances*. To obtain a resistance, we solve the equations describing a system as if all other processes were turned off. Once we have cycled through each of the physically limiting processes, with all other processes turned off, we will have formed the basis set of resistances required to model the overall process. The fundamental assumption is that we may closely approximate a description of physical reality (almost always involving some degree of nonlinear inter-couplings of processes) through a simple decoupled superposition of the basis resistances. In the resistor analogy, used here for mass transfer and chemical reaction, processes can add either in series or in parallel. Series processes are those that vanish if any one element vanishes, whereas parallel processes occur along simultaneous channels. For example, gas phase diffusion and mass accommodation (see below) are in series with one another since either one's absence makes mass transfer into the particle impossible. This formulation has been tested in previous studies, although not encompassing combinations of all the various resistances considered here. Solutions to limiting processes such as gas phase diffusion, mass accommodation, solubility, and chemical reactions have been presented in the literature[8,9]. Using such available analytical solutions to form appropriate resistances, approximate expressions for overall processes have been formulated. This decoupled formulation has been shown to be in good agreement (within about 15%) with analytically coupled solutions where these are available[2,10].

4.2 The model

We envision five fundamental processes that form the basis elements of the model. 1) The gas phase molecule must first diffuse to the aerosol surface where it can collide with and thermally accommodate onto the surface with probability S called the adsorption or thermal accommodation coefficient. The adsorbed molecule may desorb at a rate governed by the first order rate constant k_{des} or, in the case of a liquid, it may enter the bulk liquid, at a rate governed by the rate constant k_{solv}. These two rates together with thermal accommodation coefficient, S determine the mass accommodation coefficient, α, which is the probability that an atom or molecule striking the surface enters into the bulk liquid phase. 2) Reactions of the trace gas may also occur specifically on the surface of the aerosol with rates that may be different than those found in bulk. While saturating the surface, the trace species can diffuse into the aerosol bulk as it reacts with it. As the gas enters the particle, a fraction may evaporate back into gas phase due to the limited solubility of the species in the liquid (Henry's law). It is this entrance of the gas species into the particle (dependent on gas solubility, diffusivity, and reactivity) that establishes a concentration profile within the particle. 3) In the case of slow reaction or fast diffusion it will diffuse deep into the aerosol bulk, filling it to saturation. 4) In the case of fast reaction or slow diffusion it will tend to be confined to a thin shell near the surface. 5) In this case, the particle phase species must diffuse to the surface region in order to react. In relatively large or highly viscous aerosols, one may also have to take into account diffusive transport of particle-phase reactant toward the region near the aerosol surface where reactions are occurring. Each of the latter individual processes can be described by independently solving the relevant partial differential equation with appropriate boundary and initial conditions.

In experiments subject to any of these processes and/or limitations, the measured flux, J of trace gas into the surface is expressed in terms of a measured uptake coefficient, g_{meas}, as:

$$J = \frac{n_{x(g)}\bar{c}g_{meas}}{4} \tag{4.1}$$

Here $n_{X(g)}$ is the bulk concentration of the trace gas molecules (species X) and $\bar{c}$ is their average thermal speed. Of course, g_{meas} is always smaller than or equal to 1 since the flux cannot exceed the collision rate per unit area, $n_{X(g)}\ \bar{c}/4$. The model ensures that this is the case, as will be seen below.

In the case where a trace gas concentration profile has been established within the particle (shown below to be typically much faster than other processes), all the reactive gas molecules in the flux, J (as in eq. 4.1) through the aerosol surface react with the particle phase species Y. Therefore, mass balance allows us to write the volume-averaged particle phase loss rate $[\dot{Y}]$ = $d[Y]/dt$ within an aerosol of radius a, as in:

$$\frac{n_{x(g)}\bar{c}g_{meas}}{4}4pa^2 = \frac{4}{3}pa^3[\dot{Y}]$$

such that,

$$[\dot{Y}] = -\frac{3}{a}\frac{n_{x(g)}\bar{c}g_{meas}}{4} \tag{4.2}$$

In general, a, g_{meas}, and $n_{X(g)}$ will vary with time as a result of gas-particle interactions.

The goal then is to formulate an expression for g_{meas} by adding the basis resistances (taken from the various limiting processes) appropriately. In this treatment, the resistance of the i^{th} process is given by $1/\Gamma_i$, where Γ_i represents the normalized rate of process i. More specifically, Γ_i is the ratio of the flux of trace gas to the kinetic collision frequency, assuming a

Maxwell-Boltzmann distribution prevails near the aerosol surface. In the absence of solubility limitations, the overall resistance equation from which one obtains g_{meas} is written as:

$$\frac{1}{g_{meas}} = \frac{1}{\Gamma_{diff}} + \frac{1}{S} + \frac{1}{\Gamma_s + \frac{1}{\frac{S-a}{Sa} + \frac{1}{\Gamma_{rxn}}}} + \frac{1}{\Gamma^p{}_{diff}} \tag{4.3}$$

and shown in fig. 4-1. Because the adsorption coefficient *S*, is ≤ 1 the maximum value of g_{meas} is limited to unity. There is no limit to the value of the Γ terms.[a]

The 1/Γ terms in eq. 4.3 (and fig. 4-1) represent gas phase diffusion (Γ_{diff}), surface reaction (Γ_s), mass accommodation (α), chemical reaction within in the particle (Γ_{rxn}) and diffusion limited mixing within the particle ($\Gamma^p{}_{diff}$). These terms account for process rates (and concentration gradients) in the gas phase, at the interface and within the particle. Taken together, they form the basis of the general model. The term $\Gamma^p{}_{\mathrm{diff}}$, which accounts for the diffusion limited gradient of the reactant *Y* within the particle, is presented here for the first time. This formulation assumes that the aerosol consists of a single component *Y*. We note that in modeling multi-component aerosols, separate Γ_{rxn}, Γ_s, and $\Gamma^p{}_{diff}$ need to be formulated for each component.

When one is concerned with the depletion of gas phase species or when solubility dynamics are expected to influence the overall rate, a time dependent solubility term $1/\Gamma_{\mathrm{sol}}$ is added in parallel with the $1/\Gamma_{rxn}$ term. Alternatively (see below) this can be included in a more complicated form of $1/\Gamma_{rxn}$, for which an analytical solution has been derived in the literature. We will show below why the term $1/\Gamma_{\mathrm{sol}}$ is not expected to affect particle species reactive loss.

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[a] In the limit of high Γ, the resistance goes to zero.

Also, the trace gas (n_x) that is simply solvated in the particle phase does not result in particle species loss. Therefore, since the purpose of this presentation is to develop expressions for particle species reaction rate [$\dot{Y}$], the term $1/\Gamma_{sol}$ has been omitted from eq. 4.3.

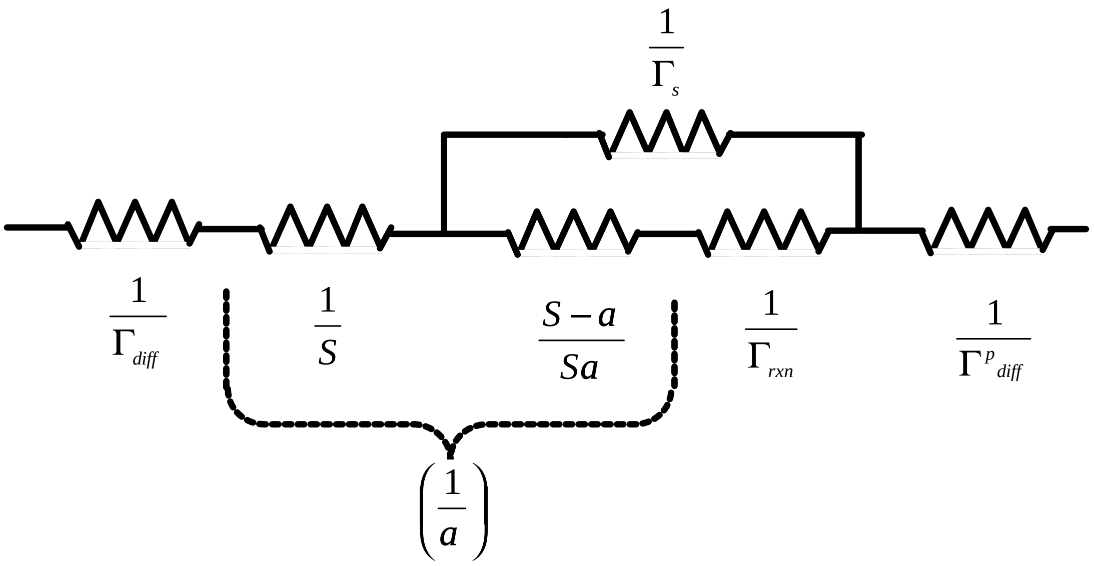

Figure 4-1: Electrical circuit analogue for the gas uptake process governed by gas-phase diffusion, mass accommodation, surface reactions, and particle phase reaction and diffusion.

4.2.1 Gas phase diffusion and mass accomodation

When gas phase diffusion or mass accomodation is limiting, the rate of processing within the aerosol will be governed by how quickly the gas diffuses to and passes through the surface of the aerosol. An empirical formulation of isothermal diffusive transport[11] that is in good agreement with experimental data[12] can be written as the resistance $1/\Gamma_{diff}$ [13]:

$$\frac{1}{\Gamma_{diff}} = \frac{0.75 + 0.283Kn}{Kn(1+Kn)} \tag{4.4}$$

where Kn is the Knudsen number defined as l/a and l is the gas phase mean free path. The mean free path is here expressed as $l = 3D_{X(g)}/\bar{c}$, where $D_{X(g)}$ is the gas phase diffusion coefficient of the trace species. As shown schematically in fig. 4-1, $1/\Gamma_{diff}$ represents the "resistance" of gas phase diffusion to the gas uptake, accounting for the gradient in gas phase concentration due to the flux of gas into the particle.

As described in detail previously[2], interfacial resistance to mass transport can be formulated in terms of the mass accommodation coefficient, α, which can be expressed as:

$$\frac{1}{\alpha} = \frac{1}{S} + \frac{k_{des}}{Sk_{sol}} \quad or \quad \frac{k_{des}}{Sk_{sol}} = \frac{S-\alpha}{S\alpha} \tag{4.5}$$

The ratio k_{sol} / k_{des} is the true measure of the interfacial kinetic resistance, though α is often quoted as the collision probability coefficient for trace gas uptake into the (liquid) particle.

4.2.2 Surface reactions

Once the trace gas X has diffused to the surface, it can react with aerosol species Y directly at the surface via a mechanism that is kinetically separable from reaction within the particle. As shown in fig.1, this corresponds to a "resistance" term between $1/S$ and $k_{des}/Sk_{sol} = (S-\alpha)/S\alpha$ (see eq. 4.5), since such surface reactivity competes with mass accommodation of X into the bulk particle through the gas/surface interface. We use the same approach here to find Γ_s as in the case of gas phase diffusion. We calculate gas phase flux into the particle, assuming that this specific process is solely the one governing the uptake.

Here we suggest the following expression for the surface reaction rate between species X and Y per unit area per second:

$$\frac{n_{x(g)}\bar{c}\Gamma_s}{4} = k_2^s[X]_s[Y]_s = k_2^s n_{x(g)} H_s RT[Y]_s \tag{4.6}$$

In eq. 4.6 we have assumed that the surface concentration of trace species is in equilibrium with the gas phase, analogous to a Henry's law equilibrium for bulk condensed phases. All surface concentrations are in moles cm^{-2} and H_s and k^s_2 are surface analogs to their bulk counterparts. Alternate formulations of eq. 4.6 may be more convenient in some cases (see *Hu et al.*, [1995][14]). Using the above formulation with the further assumption that $[Y]_s = K_s[Y]$, we may write the uptake coefficient Γ_s from eq. 4.6:

$$\Gamma_s = \frac{4k_2^s H_s RTK_s[Y]}{\bar{c}} \tag{4.7}$$

Here, K_s is an equilibrium constant (with units of L cm^{-2}) linking the surface concentration $[Y]_s$ to the bulk concentration $[Y]$. The equilibrium parameters H_s and K_s used in eq. 4.7 can at times be obtained experimentally from surface tension measurements for example, or can be estimated by extrapolation from bulk phase equilibrium values.

4.2.3 Reactions within the particle interior

For the simultaneous reaction and diffusion of the trace gas into the aerosol, we hold the trace species concentration constant at the surface, while allowing the trace gas to react as it diffuses into the aerosol. Because this process is expected to be important in laboratory and field studies, we will derive it here in detail. We begin with the diffusion equation including an additional term for reaction within the particle:

$$D_{x(p)}\nabla^2[X](r,t) - k_2[X](r,t)[Y] = [\dot{X}](r,t) \tag{4.8}$$

This expression takes into account the full dynamics of trace gas species diffusion, solubility, and reaction within the particle. It does not explicitly account for the loss of Y due to reaction with X, which would require a mirror equation of eq. 4.8 for Y. For now we will make a simplifying assumption that we will justify below: The initial profile $[X](r)$ is established so quickly, that we can assume the loss rate of Y to be governed by the pseudo-steady state profile of X within the particle. In other words, after some very brief moment, $[X](r)$ develops, establishing a volume-averaged loss rate of particle species given by:

$$[\dot{Y}] = \frac{3}{4pa^3}\int_0^a k_2[X](r,t)[Y](t)4pr^2 dr \tag{4.9}$$

In this expression we write $[X](r,t)$, explicitly a function of time, not due to the dynamics in eq 4.13, but because depletion of Y changes the steady state profile of X. Making the assumption that eq. 4.13 is at steady state allows us to write it as:

$$D_{x(p)}\nabla^2[X](r) - k_2[X](r)[Y] = 0 \tag{4.10}$$

or in spherical coordinates:

$$\frac{d^2[X](r)}{dr^2} + \frac{2}{r}\frac{d[X](r)}{dr} - \frac{k_1}{D_{x(p)}}[X](r) = 0 \tag{4.11}$$

Here, $k_1 = k_2[Y]$.

The analytical solution, describing the trace-gas concentration within the particle as a function of radial position and particle species concentration, can be shown to be[15]:

$$[X](r) = [X](a)\frac{a}{r}\frac{\sinh(r/l)}{\sinh(a/l)} \quad \text{where} \quad l \equiv \sqrt{\frac{D_{x(p)}}{k_2[Y]}} \tag{4.12}$$

The parameter l, is the reacto-diffusive length representing the depth to which solvated trace species X diffuses while reacting with Y. This depth reflects the distance reactant X will diffuse in one reactive characteristic time ($1/k_2[Y]$). We note that the concentration profile of X depends on the concentration of Y within the particle; X will diffuse more deeply on average into the particle the less Y there is with which it can react. It is for this reason that we refer to $[X](r)$ as a *pseudo*-steady state profile.

At any instant in time, the net rate at which species X enters the particle equals the rate at which species Y is depleted. Also, by definition this must be equal to the volume-averaged reaction rate within the particle itself, given by eq. 4.9. Using Fick's law to access the net flux of reactant gas molecules at the surface we have:

$$J_x = -D_{x(g)} \frac{d[X](r)}{dr}\Big)_{r=a} = \frac{n_{x(g)}\bar{c}\Gamma_{rxn}}{4} \tag{4.13}$$

such that we may write Γ_{rxn} as:

$$\Gamma_{rxn} = \frac{4HRT}{\bar{c}}\sqrt{D_{x(p)}k_2[Y]}\left[\coth(a/l)-(l/a)\right] \tag{4.14}$$

In this expression, we have replaced [X](a) with the Henry's law value, $HP_x = Hn_{x(g)}/RT$. Here $D_{x(p)}$ is the diffusion coefficient of the solvated trace species X in the particle phase, H is its Henry's law coefficient (H is in units M atm^{-1} L^{-1}, R is the gas constant in matching units), and k_2 is the second order rate coefficient for the reaction of X with Y. In fig. 4-2, we show how this function depends functionally on l and a. This is the same expression as presented in Hanson and Lovejoy[1], where it was first applied to aerosol kinetics.

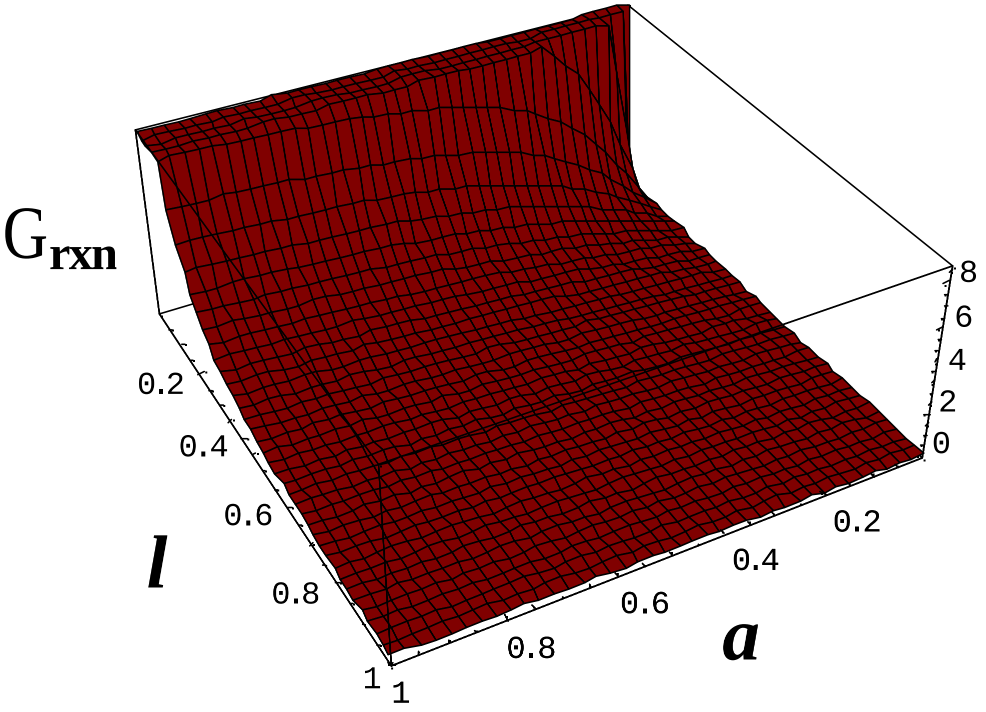

Figure 4-2: General functional dependence of reactive uptake coefficient on particle radius, *a* and reacto-diffusive depth, *l*.

4.2.4 Particle phase diffusion

As we have seen in the case of rapid reaction, it is possible that the trace gas diffuse to a depth many times smaller that the particle radius. Most of the aerosol chemical processing will occur within this reacto-diffusive length, *l*. If diffusion of particle species to this reaction region is sufficiently slow, the overall rate of processing can be expected to decrease due to a depletion of particle species concentration in this region.

Here we derive an exact expression for the resistance when the diffusion of the particle phase species is many times slower than reaction near the surface. Thus the rate at which particle phase molecules disappear from the particle will be governed entirely by how quickly they can diffuse to the surface where they immediately react away. In this case the surface concentration of the particle phase species is zero by construction; the particle phase molecule is destroyed by reaction the very instant it reaches the surface region. This process is taken into account by the coefficient $\Gamma^{p}{}_{diff}$, the last term shown in eq. 4.3 and fig. 4-1. We derive an expression for $\Gamma^{p}{}_{diff}$ here for the first time.

We assume that the reactive gas phase flux into the aerosol is governed by the diffusion rate of *Y* from the particle interior. Matching the trace gas flux through the surface to the flux of *Y* toward the surface we have:

$$\frac{n_{x(g)}\bar{c}\,\Gamma^{p}{}_{diff}}{4} = D_y \, \frac{\partial [Y](r,t)}{\partial r})_{r=a} \qquad (4.15)$$

A solution to the diffusion equation in spherical coordinates can be found through separation of variables. Subject to the boundary condition that [*Y*] = 0 at the particle surface and [*Y*] = $[Y]_0$ initially everywhere within the particle, an exact expression for [*Y*](*r*,*t*) is found to be[16] (see fig. 4-3):

$$\frac{[Y](r,t)}{[Y_0]} = \frac{2a}{pr} \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{n} \sin\frac{npr}{a} \exp(-D_y n^2 p^2 t / a^2) \qquad (4.16)$$

Through eq. 4.2, (with some work) we may now write:

$$\Gamma^{p}_{diff} = \frac{8D_y[Y]_0}{an_x\bar{c}}\sum_{i=1}^{\infty} Exp(\frac{-iD_y p^{2} t}{a^{2}}) \tag{4.17}$$

A significantly simpler expression for $\Gamma^{p}{}_{diff}$ can be obtained by assuming a linear concentration profile for Y, as $[Y](r) = [Y_c](1 - r/a)$, where $[Y_c] = [Y](r=0)$. Therefore, $d[Y](r)/dr = -[Y_c]/a$. From the definition of the average concentration, we have:

$$[Y] \equiv \frac{3}{4pa^{3}}\int_{0}^{a}[Y](r)4pr^{2}dr = \frac{[Y_c]}{4} \tag{4.18}$$

Combining expressions, the simplified expression for $\Gamma^{p}{}_{diff}$ emerges as,

$$\Gamma^{p}{}_{diff} = \frac{16D_y}{n_{x(g)}\bar{c}}\frac{[Y]}{a} \tag{4.19}$$

This simple expression is in a form consistent with the other uptake coefficients and lends itself to facile computation. The accuracy of this expression will be discussed later. The uptake coefficient $\Gamma^{p}{}_{diff}$ becomes important (i.e. $1/\Gamma^{p}{}_{diff}$ is large) in the limit of large, highly viscous particles, where diffusion of Y from within the bulk of the particle must compete with surface or near surface reaction, leading to a gradient in $[Y](r)$ within the particle.

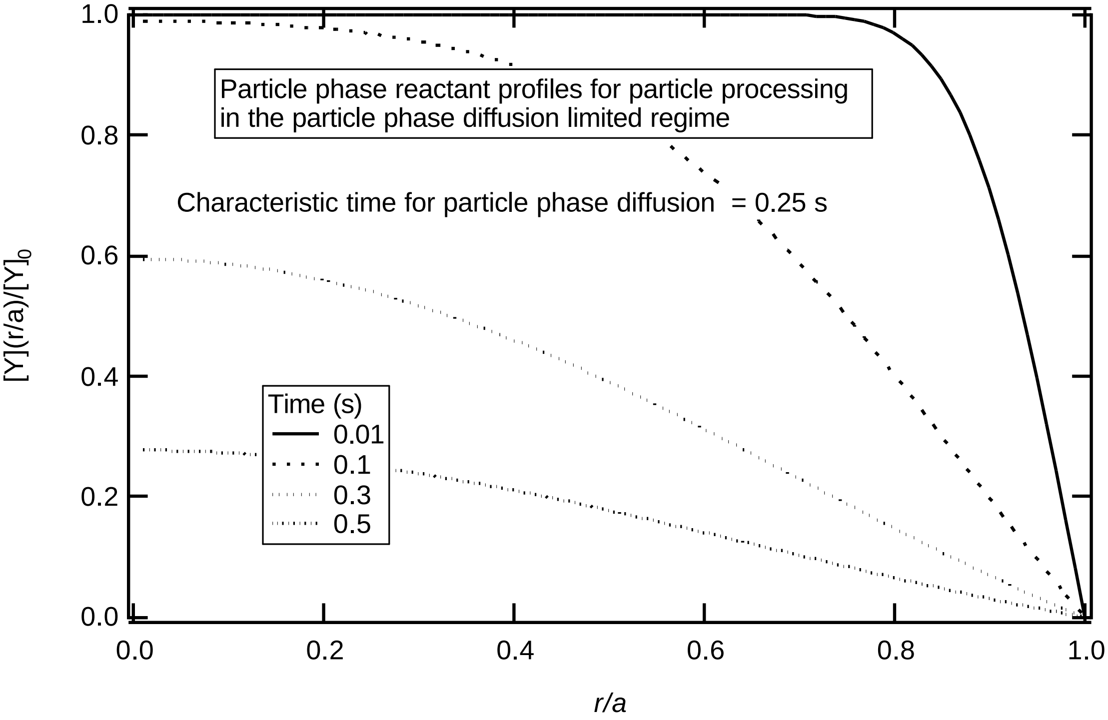

Figure 4-3: Particle phase concentration profiles as a function of time in a particle reacting in the particle-phase diffusion limited regime.

Limiting process	**Gamma**	**Tau**	**Size dependence of rate d[Y]/dt**	**Criteria for importance**
Gas phase diffusion	$\frac{Kn(1+Kn)}{0.75+0.283Kn}$	$\frac{a^2}{p^2 D_{x(g)}}$ ~ 10^{-8} s	a^{-1} *to* a^{-2}	Very large particles
Mass accomodation	a	$\frac{aH\sqrt{2pMRT}}{3a}$ ~ 10^{-7}	a^{-1} *to* a^{-2}	Large particles, soluble trace gas, low α
Surface reaction	$\frac{4k_2{}^s H_s RTK_s[Y]}{\bar{c}}$	$\frac{a}{3k_2{}^s H_s P_x K_s}$	a^{-1}	See resistor model
Thin-shell reaction	$\frac{4HRT}{\bar{c}}\sqrt{D_{x(p)}k_2[Y]}$	$\frac{a}{3HP_x}\sqrt{\frac{[Y]}{k_2 D_{x(p)}}}$ ~ 10^0	a^{-1}	$\sqrt{\frac{D_{x,p}}{k_2[Y]}} << a$
Bulk reaction	$\frac{4aHRT}{3\bar{c}}k_2[Y]$	$\frac{1}{k_2 HP_x}$ ~ 10^{-1}	a^0	$\sqrt{\frac{D_{x,p}}{k_2[Y]}} >> a$
Particle phase diffusion	$\frac{16D_y[Y]}{n_{x(g)}\bar{c}a}$	$\frac{a^2}{p^2 D_y}$ ~ 10^{-2}	a^{-2}	Fast reaction, highly soluble trace gas and/ or very large particles

Table 4-1: Summary of gammas (inverse resistances) and characteristic times (see appendix) relevant in aerosol chemical transformations.

4.3 Particle phase loss in limiting cases

We will now apply eq. 4.2 to calculate the fraction of particle phase species Y remaining ($[Y](t)/[Y]_0$) given the initial concentration $[Y]_0$, due to interaction with gas phase reactive species X in specific limiting cases. In these calculations we will assume that the overall gas phase density $n_{x(g)}$ remains constant throughout the reaction, since atmospheric aerosol mass loadings are small, (typically on the order 10 μg m^{-3}) and therefore only a small fraction of the trace gas is expected to react. Also, while particle size change due to gas-particle interactions can be accounted for, here we will assume that the particle size remains constant. In each case shown below the functional dependence on physico-chemical parameters, particle size a, gas phase density $n_{x(g)}$, and initial particle phase concentration is clearly evident. Therefore, it is possible to establish the rate limiting process through comparison with data from a controlled experiment or well-monitored field study.

4.3.1 Particle phase loss limited by gas phase diffusion and/or mass accommodation of *X*

This is the case for very rapid (non-surface) *X*-*Y* reaction, (i.e. $\Gamma_s << \alpha$ and $\Gamma_{rxn} >> \alpha$). In other words, the species *X* is consumed as rapidly as it enters the bulk and therefore g_{meas}?= $(1/\Gamma_{diff} + 1/\alpha)^{-1}$. Upon integration of eq. 4.2 we obtain:

$$\frac{[Y](t)}{[Y]_0} = 1 - \frac{n_{x(g)}\bar{c}}{4[Y]_0}\frac{3}{a}(1/\Gamma_{diff} + 1/a)^{-1}t \tag{4.20}$$

The loss of *Y* is particle size dependent in general. In the case of kinetic flux to the particle surface, the incoming mass flow rate goes as the particle surface area (flux independent of radius), whereas the reaction takes place throughout the bulk of the aerosol. In the case of a continuum flux into the particle, the mass flow rate goes as the radius (flux going as the inverse radius). Eq. 4.4 will have varying size dependence, depending on the regime applicable, and this will manifest in the size dependence of the particle phase loss rate (eq. 4.20).

4.3.2 Particle phase loss limited by surface reaction

This may reflect very efficient liquid surface reactivity or be effectively true when concentrations near the surface are larger than their bulk values (i.e. Gibb's surface excess). In this case $g_{meas} = \Gamma_s$ as given by eq. 4.11 and via integration of eq. 4.2:

$$\ln\frac{[Y](t)}{[Y]_0} = -\frac{3H_s RTn_{x(g)}K_s k_2^s}{a}t \tag{4.21}$$

4.3.3 Particle phase loss limited by reaction within short reacto-diffusive length, *l* << *a*

In this case, reaction of *X* and *Y* occurs in a thin shell of depth *l* below the aerosol surface. When *l*<<*a*, the *coth* term in eq. 4.14 approaches 1, and we are left with:

$$\Gamma_{rxn} = \frac{4HRT}{\bar{c}} \sqrt{D_{x(p)} k_2 [Y]} \tag{4.22}$$

Now with $\gamma_{meas} \overset{?}{=} \Gamma_{rxn}$ integration of eq. 4.2 yields:

$$\sqrt{\frac{[Y](t)}{[Y]_0}} = 1 - \frac{3RTn_{x(g)} H \sqrt{D_{x(p)} k_2}}{2a\sqrt{[Y]}_0} t \tag{4.23}$$

We note that this expression breaks down in the limit where [*Y*]->0, since here *l* is no longer much less than *a*. Realizing this physical limitation obviates concerns of the long time solution (leading to increasing [*Y*](t)), clearly beyond the domain of applicability of the expression.

4.3.4 Particle phase loss limited by reaction within long reacto-diffusive length, *l* >> *a*

In the limit where *l* >> *a*, the *coth* term approaches *l/a* + *a/3l*. This is consistent with the trace gas having very quickly filled the particle to its Henry's law concentration (that is, [*X*] = $n_{x(g)}HRT$). In this case eq. 4.14 reduces to:

$$\Gamma_{rxn} = \frac{4aHRT}{3\bar{c}} k_2 [Y] \tag{4.24}$$

Now with $\gamma_{meas} \overset{?}{=} \Gamma_{rxn}$, integration of eq. 4.2 yields:

$$\ln \frac{[Y](t)}{[Y]_0} = -HRTn_{x(g)} k_2 t \tag{4.25}$$

4.3.5 Particle phase loss limited by diffusion of *Y* from the aerosol interior toward the surface

In this case $g_{meas} = \Gamma^{p}_{diff}$. Using the simplified expression for Γ^{p}_{diff} given by eq. 4.19, upon integrating eq. 4.2 one obtains:

$$\ln\frac{[Y](t)}{[Y]_0} = -\frac{12D_y}{a^2}t \qquad (4.26)$$

Dependence on particle size is here second order. Further, this is the only case where the fraction remaining is independent of $n_{x(g)}$. We anticipate this physically since adding more trace gas will not affect the processing rate when mass transfer within the particle is solely rate limiting. Eq. 4.26 reflects the maximum decay rate of *Y*, dependent only on the rate of diffusion of *Y* within the particle. Thus, in the absence of convective mixing within the particle, eq. 4.26 sets an overall upper limit for the chemical transformation rate within aerosols. This case is rate controlling in the limit of large or highly viscous particles and in the limit of fast $X + Y$ reaction that locally depletes [*Y*] at or below the surface of the particle.

A solution for particle phase concentration using the more exact expression for Γ^{p}_{diff} (eq. 4.17) can also be derived[17]:

$$\frac{[Y](t)}{[Y]_0} = \sum_{i=1}^{\infty}\frac{6}{p^2 i^2}\exp\left(\frac{-i^2 p^2 D_y t}{a^2}\right) \qquad (4.27)$$

However, a smooth function requires the summation of about 100 terms. Eq. 4.26 overestimates $[Y]/[Y]_0$ at 0.50 and 0.10 fraction remaining by 32% and 10% respectively. At 0.05 fraction remaining eq. 4.26 is within 1% of the exact solution. This is shown in fig. 4-5.

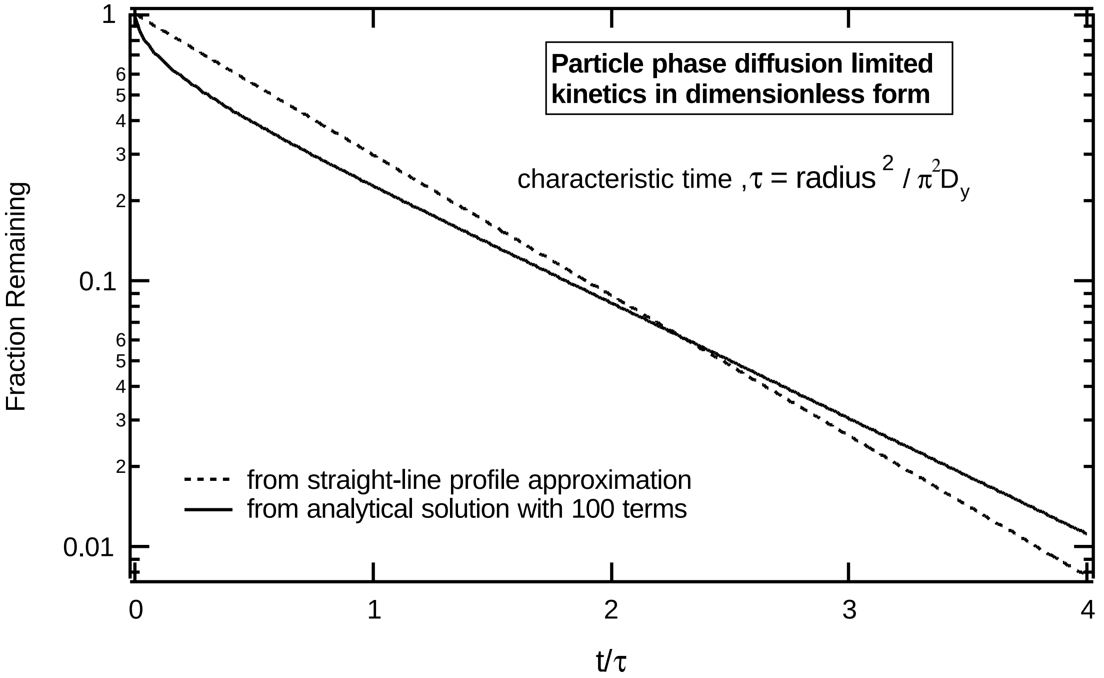

Figure 4-5: Comparison of kinetics based on straight-line concentration profile and those based on analytical solution in the case of the particle phase diffusion limit.

4.4 Simultaneous reaction and particle phase diffusion

The general problem of combined reaction and diffusion of both the trace gas and the particle phase species within the particle is mathematically described through the following system of partial differential equations:

$$D_{x(p)}\nabla^2[X](r,t) - k_2[X](r,t)[Y](r,t) = [\dot{X}](r,t)$$

$$D_{y(p)}\nabla^2[Y](r,t) - k_2[X](r,t)[Y](r,t) = [\dot{Y}](r,t) \qquad (4.28)$$

Taken with four boundary conditions (to satisfy the four spatial derivatives) and two initial conditions (to satisfy the two time derivatives) eqs. 4.28 fully define the physical process. However, no known analytical solution exists for this system. We will therefore apply the method of resistances to obtain an approximate solution. We will couple particle phase diffusion with reaction characterized by short reacto-diffusive length. Once in possession of a solution we will compare it to an analytical solution that is expected to approximate the actual solution closely. A more rigorous comparison can be pursued using advanced numerical techniques.

Particle phase diffusion and thin shell reaction are expected to dominate particle phase loss simultaneously when their characteristic times are within an order of magnitude of one another while each is at least two orders of magnitude higher (slower) than those for all other processes. Mathematically we expect:

$$\frac{t_{rxn,l<<a}}{t_{diff}{}^{p}} = \frac{p^{2} D_{y}}{3HP_{x}a}\sqrt{\frac{[Y]}{k_{2}D_{x(p)}}} \sim 1 \qquad (4.29)$$

It is therefore expected to be important for large particles whose self-diffusion coefficient is very low, in the presence of highly soluble and highly reactive trace gas. In cases where the above ratio is near unity, we will need to use the resistor model to approximate the overall particle phase loss rate. We develop an expression for γ_{meas} by combining Γ_{rxn} (with *l*<<*a*, eq. 4.34) and Γ^{p}_{diff} (eq. 4.30). This enables us to use eq. 4.2 and write:

$$[\dot{Y}] = \frac{-12[Y]D_{y}P_{x}H\sqrt{D_{x(p)}k_{2}}}{a(4D_{y}\sqrt{[Y]} + aP_{x}H\sqrt{D_{x(p)}k_{2}})} \qquad (4.30)$$

Integration of this expression at the limits recovers eq. 4.26 and eq. 4.23 as expected. The general analytical solution of eq. 4.30 is quite cumbersome[13], but solving it through numerical integration using either Runge-Kutta or Euler schemes is straightforward.

Comparison of resistor model result with an analytical solution

In our resistor model formulation, we have allowed for the fact that as the reaction ensues, the reacto-diffusive length increases. Though a general analytical solution for eqs. 4.28 does not exist, in the case where we hold *l* constant a solution can be found by appropriately changing the boundary conditions to a previously solved problem. Since we confine the reaction to a thin shell near the surface, in the particle interior we have simple diffusion, or:

$$D_y \left(\frac{\partial^2 [Y](r,t)}{\partial r^2} + \frac{2}{r}\frac{\partial [Y](r,t)}{\partial r}\right) = \frac{\partial [Y](r,t)}{\partial t} \tag{4.31}$$

At the boundary, which we for convenience define as the surface lying a constant depth l_0 beneath the surface, we require that the flux of particle phase species from the bulk match the rate of disappearance due to reaction in the shell. Our first boundary condition is therefore:

$$-D_y \frac{\partial [Y]}{\partial r}\Big)_{r\sim a} = HP_x k_2 [Y](a) l_0 \quad l_0 \equiv \sqrt{\frac{D_{x,p}}{k_2 [Y]_0}} \tag{4.32}$$

The second boundary condition requires the concentration gradient vanish at $r = 0$:

$$\frac{\partial [Y]}{\partial r}\Big)_{r=0} = 0 \tag{4.33}$$

The initial condition is:

$$[Y](r,0) = [Y]_0 \tag{4.34}$$

These conditions are analogous to those in the *surface evaporation* case for which a solution is provided in the literature, and a solution can be adapted to our case of thin shell reaction[18]:

$$\frac{[Y]}{[Y]_0}(t) = \sum_{n=1}^{\infty} \frac{6L^2 \exp(-b_n D_y t / a^2)}{b^2_n \left\{ b^2_n + L(L-1) \right\}} \quad L \equiv \frac{aHP_x k_2 l_0}{D_y} \tag{4.35}$$

Here, the β_n must be solved for numerically (i.e. using bisection or the Newton-Raphson technique) from:

$$b_n \cot b_n + L - 1 = 0 \tag{4.36}$$

In fig. 4-6 we compare this analytical result to the resistor model approximation.

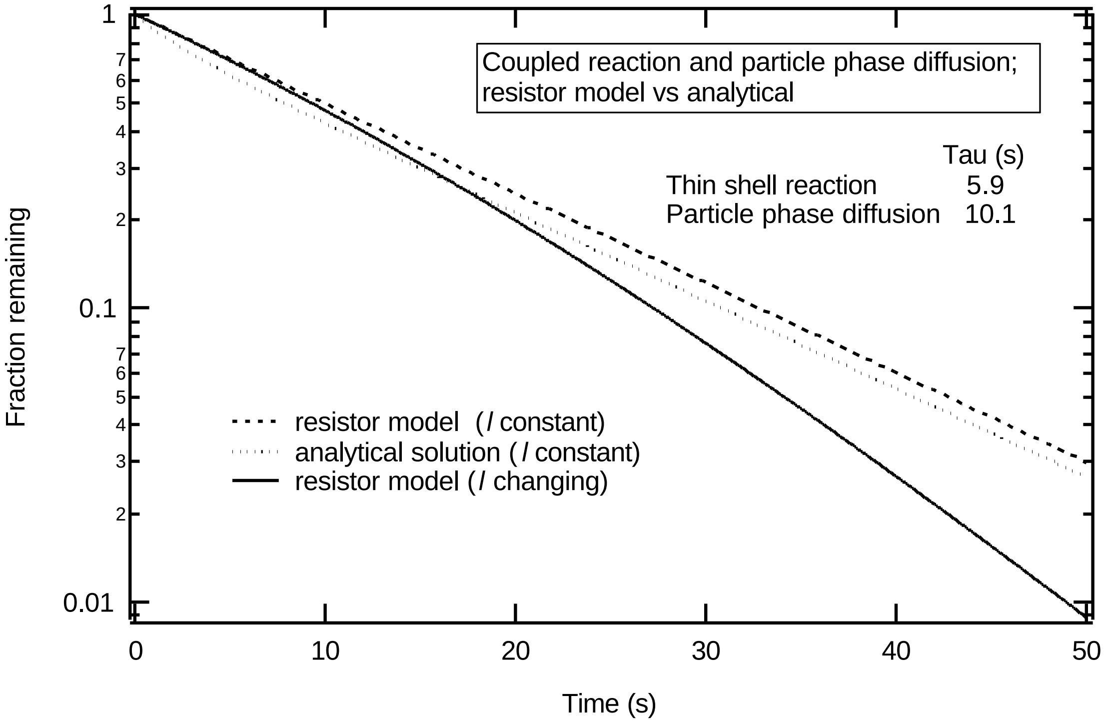

Figure 4-6: Comparison of resistor model with analytical solution in the case of constant reacto-diffusive length. The changing reacto-diffusive length result is also shown for comparison. Calculations were performed on a 10 micron particle with physico-chemical parameters yielding characteristic times shown.

From fig. 4-6 it is evident that the resistor model result very closely matches the more complicated analytical solution for the case where we hold the reacto-diffusive length constant. The resistor model result for *l* changing matches the analytical solution at early times, but delivers smaller fractions remaining at longer times. This reflects the fact that as the reacto-diffusive depth increases, the reaction takes place throughout a larger volume, and thus results in a higher overall loss rate.

4.5 Application of results

The interest in aerosol particle-phase chemical transformation is relatively recent. To our knowledge there are only a few studies illustrating the reactive regimes discussed above. In laboratory studies of sub-micron (0.2 to 0.6 μm) aerosol ozonolysis, the reactive depletion of oleic acid clearly matched Case 4.3.3 (see ch. 5, below), exhibiting the predicted reactant concentration and aerosol size dependence[5]. In a similar experiment with larger oleic acid aerosols (0.68 to 2.5 μm), the Miller research group at the University of North Carolina observed transition from Case 4.3.3 to Case 4.3.5 as the aerosol size increased (submitted for publication). Both experiments yielded oleic acid/ozone transformation rates much faster than deduced from atmospheric field studies[19], indicating that atmospheric reactivity depends on the morphology of complex particles. In an earlier study focusing on reactive gas uptake, Hanson and Lovejoy [1995] observed uptake kinetics governed by Cases 4.3.2 and 4.3.3. With the advent of single particle aerosol mass spectrometers, field data quantifying the time and/or distance dependence of aerosol chemical composition will become much more common, and models incorporating particle phase reactions using the formulation presented here will be required to interpret many of these studies.

Chapter 4 Appendix

A4.1 Characteristic times for limiting processes

Obtaining characteristic times for these processes is pursued in a manner similar to that used in deriving individual resistances. One solves the partial differential equations relevant to the process assuming it alone is acting. The solution will typically contain an exponential summation of the form:

$$\sum_{j=1}^{\infty} \exp(- jf(p_i)t) \qquad \text{(A4.1)}$$

Here $f(p_i)$ is a function of the physico-chemical parameters, p_i (i=1,2,3…) characterizing the particular process. The characteristic time is then expressed as[b] $t = 1/f(p_i)$. It follows that for $t >> t$, the exponential terms are vanishingly small, and the dynamics are expectedly very slow (very long times are required to see very small changes in the system). The system here is described as being "relaxed". On the other hand, for $t << t$, the system exhibits very large changes in very small increments of time. The characteristic time then gives us an approximation of the relaxation time of the system, dividing the regions of fast and slow dynamics. Given estimates of the characteristic times for various processes, the process with the slowest characteristic time is the one most likely to govern the overall rate.

A4.1.1 Gas phase diffusion and mass accomodation

The characteristic time for gas phase diffusion in the continuum regime (Kn <<1) is taken from the time-dependent solution of the diffusion equation and approximates the time for the concentration profile around the aerosol to achieves a steady state value:

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[b] For systems of sufficient simplicity it may not be necessary to solve for eq. A4.1. For example, first order ordinary differential equations describing many kinetic phenomena have characteristic times given by $t=[Y]/[\dot{Y}]$.

$$t_{g,diff} = \frac{a^2}{p^2 D_{x(g)}} \qquad \text{(A4.2)}$$

In this expression $D_{x(g)}$ is the diffusion coefficient (cm^2 s^{-1}) of the trace gas around the particle.

The characteristic time for mass accomodation (sometimes called the characteristic time for interfacial equilibrium) indicates the timescale over which the species taken up by the surface obtains its equilibrium concentration value there. We are describing a case where an aerosol initially devoid of trace gas is suddenly plunged into a known concentration of trace gas, held constant during the uptake process. The characteristic time[c] emerging from the time-dependence of the analytical solution is[20]:

$$t_{ie} = \frac{aH\sqrt{2pM_x RT}}{3a} \qquad \text{(A4.3)}$$

In the special case of highly insoluble trace gas, the characteristic time becomes:

$$t_{ie,insol} = \frac{a^2}{p^2 D_{x(p)}} \qquad \text{(A4.4)}$$

In these expressions, H is Henry's law solubility coefficient (M atm^{-1}), R is the gas constant (atm M^{-1} K^{-1}), M_x is the molecular weight of the trace species (g mole^{-1}) and $D_{x(p)}$ is the diffusivity of the trace gas in the particles.

4.2.2 Surface reactions

In this case we have only to solve an ordinary differential equation, and there is only one term in the form given in eq. A4.1. From the solution (see eq. 4.21), the characteristic time for surface reaction is:

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[c] The same expression can be derived much more simply by assuming a constant flux to the surface and calculating the time required to fill the particle to its Henry's law concentration.

$$t_s = \frac{a}{3k_2^s H_s RTK_s n_{x(g)}} \qquad \text{(A4.5)}$$

4.2.3 Reactions within the particle interior

Here we can go back to eq. 4.8 and take characteristic times from the more general solution, describing the approach to steady state. From the solution to eq. 4.8 in spherical coordinates[21], it can be shown that the characteristic time as defined through eq. A4.1 is given by:

$$t_{rxn,diff} = \frac{1}{k_2[Y] + \frac{p^2 D_{x(p)}}{a^2}} \qquad \text{(A4.6)}$$

This is the time required for *X* to approach a pseudo-steady state profile within the particle. It can therefore be thought of as a reacto-diffusive solubility time. An important question is whether the time it takes to form the profile in *X* can ever be expected to affect the overall rate of mass transfer within atmospheric particles. We will return to this question below.

In the case of a very short reacto-diffusive length, $l \ll a$, we can derive a characteristic time for reaction of *Y* within the particle using the expression in footnote (a) above. Since reaction is confined to within the shell of thickness *l*, the volume averaged loss rate of *Y* can be approximated as:

$$[\dot{Y}] = \frac{1}{\frac{4}{3}pa^3} k_2[X][Y]4pa^2 l \qquad \text{(A4.7)}$$

Taking the trace species concentration in the shell to be near its Henry's law value, this leads to an estimated characteristic time for depletion of the liquid species within the liquid shell as:

$$t_{rxn,l<<a} = \frac{[Y]}{[\dot{Y}]} = \frac{a}{3k_2HP_xl} \sim \frac{a}{3HP_x}\sqrt{\frac{[Y]}{D_{x(p)}k_2}} \tag{A4.8}$$

Since the loss rate goes as the inverse of the characteristic time, this expression indicates that particle phase loss limited by reaction within the reacto-diffusive length will exhibit inverse radius dependence.

A similar approach can be used to derive the characteristic time in the case where the trace gas fills the entire particle (or by inspection of eq. 4.36 below). One finds:

$$t_{rxn,l>>a} = \frac{1}{k_2HP_x} \tag{A4.9}$$

In this case, the loss rate is independent of size. From consideration of the characteristic times in the limiting regimes of bulk and thin shell reaction, it is apparent that when Γ_{rxn} governs the overall rate, the size dependence spans a^0 to a^{-1} depending on the extent to which the reacting trace gas penetrates into the particle interior.

We may now return to the question of the importance of reactive solubility of the trace gas in determining the overall rate of chemical transformation within particles. In the limit of very small particle radii, the characteristic time for reactive solubility, eq. A4.6, becomes:

$$t_{rxn,diff} \rightarrow \frac{a^2}{p^2D_{x(p)}} \quad a << \sqrt{\frac{p^2D_{x(p)}}{k_2[Y]}} \tag{A4.10}$$

Whereas in the limit of very large radii, we obtain:

$$t_{rxn,diff} \rightarrow \frac{1}{k_2[Y]} \quad a >> \sqrt{\frac{p^2D_{x(p)}}{k_2[Y]}} \tag{A4.11}$$

In the small particle limit, we may compare eq. A4.10 and eq. A4.12 below. Since it is unlikely that the trace gas diffusion coefficient within the particle be less than the self-diffusion coefficient of the particle species, it is unlikely that this process limit the overall rate for small sizes, since particle phase diffusion will limit instead. For very large particles, consider expressions A4.11 and A4.9 above. Since it is very unlikely that the trace species concentration ever surpass that of the particle phase, it is unlikely that this process ever limit the rate for large particles. We may infer from these limits that the same will hold for intermediary sizes, such that solubility of the reactant trace gas is unlikely to limit the overall processing rate in aerosols of atmospheric or laboratory interest.

4.2.4 Particle phase diffusion

Inspection of eq. 4.27 yields the characteristic time for particle phase diffusion:

$$t_{diff}^{p} = \frac{a^2}{p^2 D_y} \tag{A4.12}$$

We note that characteristic times allow one to quickly assess the relative importance of the five rates involved in aerosol processing, while indicating what physical parameters will likely be gained from dynamic information of the uptake process (Fig. A4-1). If for example the time for reaction of the liquid species in a thin shell is the greatest of all the characteristic times, one can expect the overall reaction rate to depend on the size (slower for larger particles) and to extract fundamental information in the form of $H(D_{x(p)}k_2)^{1/2}$**.** Table 4-1 summarizes the results presented here.

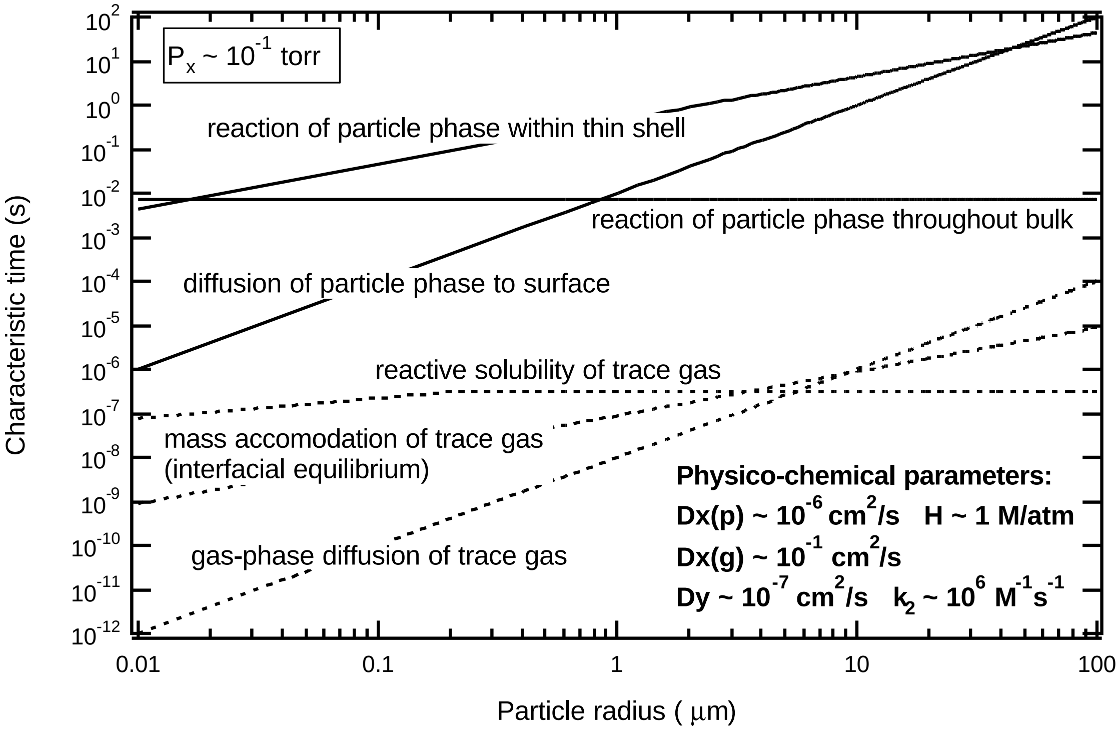

Figure A4-1. Characteristic time plot to assess competing rates. Reaction within a thin shell characteristic of the trace gas' reacto-diffusive length governs the overall rate of reaction from 0.1 to 5 micron radius particles with anticipated size dependence.

Chapter 4 References

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[1] D. R. Hanson and E. R. Lovejoy, *Science*, **267**, 1326 (1995).

[2] Q. Shi, P. Davidovits, J.T. Jayne, D. R. Worsnop, and C. E. Kolb, *J. Chem. Phys. A*, **103**, 8812 (1999).

[3] C. E. Kolb, P. Davidovits, J. T. Jayne, Q. Shi, and D. R. Worsnop, *Progress in Reaction Kin. and Mech*., **27**, 1-46 (2002).

[4] J. A. de Gouw and E. R. Lovejoy, *Geophys. Res. Lett.*, **25**, 931 (1998).

[5] J. W. Morris, P. Davidovits, J. T. Jayne, Q. Shi, C. E. Kolb, D. R. Worsnop, W. S. Barney, J. Jiminez, and G. R. Cass, *Geophys. Res. Lett.*, **10** (2002).

[6] S. E. Schwartz and J. E. Freiberg, Mass-transport considerations pertinent to aqueous phase reactions of gases in liquid-water clouds, in *Chemistry of Multiphase Atmospheric Systems*, (Springer, Heidelberg, 1984).

[7] D. R. Worsnop, J. W. Morris, P. Davidovits, Q. Shi, and C. E. Kolb, *Geophysical Research Letters*, October, 2002.

[8] P.V. Danckwerts, *Gas-Liquid Reactions*, (McGraw Hill, New York, 1970).

[9] J. Crank, *The Mathematics of Diffusion*, (Clarendon Press, 1997).

[10] D. R. Hanson, *J. Phys. Chem. B*, **101**, 4998 (1997).

[11] N. A. Fuchs and A. G. Sutugin, *Highly Dispersed Aerosols*, (Ann Arbor Science Publishers, Ann Arbor, 1970).

[12] J. F. Widmann and E. J. Davis, *J. Aerosol Sci*., **28**, 87 (1997).

[13] D. R. Hanson, A. R. Ravishankara, and E. R. Lovejoy, *J. Geophys. Res*., **101**, 9063 (1996).

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[14] J. H. Hu, Q. Shi, P. Davidovits, D. R. Worsnop, M. S. Zahniser, and C. E. Kolb, *J. Phys. Chem.*, **99**, 8768-8776 (1995).

[15] MATHEMATICA 4, Student Version.

[16] Crank, p. 91.

[17] Crank, p.107.

[18] Crank, p. 96.

[19] W. F. Rogge, M. L. Hildemann, M. A. Mazurek, G. R. Cass, and B. R. T. Simoneit, *Environ. Sci. Technol.*, **25**, 1112 (1991).

[20] S. Kumar, *Atmos. Env*., **23,** 2299 (1989).

[21] S. E. Schwartz and J. E. Freiberg, *Atmos. Environ*., **15**,1129 (1981).