

## 9. TRANSPORT EFFECTS FOR HETEROGENEOUS REACTIONS IN THE ATMOSPHERE

---

For reaction to occur in water droplets the following steps must occur:

1. Diffusion of the gas to the droplet.
2. Transfer across water-gas interface.
3. Ionization, if it occurs.
4. Diffusion of dissolved species.
5. Chemical reaction.

All of these steps occur in series and the slowest one controls (i.e determines) the overall apparent rate of reaction. Each step is characterized by its characteristic time, i.e resistance.

<u>Characteristic time for gas diffusion</u>	- time needed for the gas to establish a steady state profile around the droplet (or particle).
<u>Characteristic interfacial transport time</u>	- time needed to establish equilibrium solubility at the interface (Henry's Law).
<u>Characteristic ionization (dissociation) time</u>	- time needed to establish equilibrium between undissociated and dissociated species.
<u>Characteristic liquid diffusion time</u>	- time needed to establish uniform concentration in the droplet.
<u>Characteristic reaction time</u>	- time needed to reduce the reactant concentration to about 1/e of its initial value.

It is important to be able to estimate these characteristic times. Let us consider them one by one.

### **Diffusion to a Droplet**

Unsteady state diffusion to a spherical droplet of radius  $R_p$  in a perfectly symmetric field is given by Ficks Second Law

$$\frac{\partial C}{\partial t} = \frac{D_g}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial C}{\partial r} \right) \tag{1}$$

where  $C(r,t)$  is the gas phase concentration of diffusing species and  $D_g$  (cm<sup>2</sup>/s) is gas phase diffusivity. Coordinate  $r$  is measured from the center of the droplet. Initially

$$t = 0 \quad C(r, 0) = C_\infty \quad r > R_p \tag{2}$$

Far away from the droplet concentration remains unperturbed at all times

$$r \rightarrow \infty \quad C(r,t) = C_\infty \quad \text{for } t \geq 0 \quad (3)$$

At the droplet surface the concentration is prescribed (determined by solubility)

$$r = R_p \quad C(R_p, t) = C_s \quad (4)$$

If we would dimensionalize the above equation, say by

$$\eta = \frac{r}{R_p}; \quad u = \frac{C-C_s}{C_s}; \quad \tau = \frac{R_p^2}{D_g}; \quad \theta = t/\tau \quad (5)$$

we get

$$\frac{\partial u}{\partial \theta} = \frac{1}{\eta^2} \frac{\partial}{\partial \eta} \left( \eta^2 \frac{\partial u}{\partial \eta} \right) \quad (6)$$

$$\theta = 0 \quad u = \frac{C_\infty - C_s}{C_s} \quad (7)$$

$$\eta \rightarrow \infty \quad u = (C_\infty - C_s)/C_s \quad (8)$$

$$\eta = 1 \quad u = 0 \quad (9)$$

and we have a problem that we solved when considering diffusion limiting reactions!

Dimensionless time,  $R_p^2 t/D_g$ , occurred naturally; hence, we know that characteristic diffusion time will be  $\tau_{gd} \propto \frac{R_p^2}{D_g}$ .

The solution of our original equation (1) for  $C_s = 0$  is:

$$\frac{C(r,t)}{C_\infty} = \left( 1 - \frac{R_p}{r} \right) + \frac{2R_p}{r\sqrt{\pi}} \int_0^{(r-R_p)/2\sqrt{D_g t}} e^{-\xi^2} d\xi \quad (10)$$

The first part is the steady state solution, as the second part vanishes as  $t \rightarrow \infty$ . How large should  $t$  be for us to neglect the transient?

The diffusion flux into the droplet is now given by:

$$J = D_g \frac{\partial C}{\partial r} = D_g \left[ \frac{R_p}{r^2} + \frac{R_p}{r\sqrt{\pi D_g t}} e^{-(r-R_p)^2/4D_g t} - \frac{2R_p}{r^2\sqrt{\pi}} \int_0^{(r-R_p)/2\sqrt{D_g t}} e^{-\xi^2} d\xi \right] C_\infty \quad (11)$$

At the droplet surface the flux is:

$$J|_{r=R_p} = D_g \left[ \frac{1}{R_p} + \frac{1}{\sqrt{\pi D_g t}} \right] C_\infty = \frac{D_g}{R_p} \left[ 1 + \frac{R_p}{\sqrt{\pi D_g t}} \right] C_\infty \quad (12)$$

If we take as characteristic diffusion time the time when unsteady state contribution to the flux is equal to the steady state one, we get

$$\tau'_{gd} = \frac{R_p^2}{\pi D_g} \quad (13)$$

Alternatively, we can choose (Seinfeld)

$$\tau_{gd} = \frac{R_p^2}{4D_g} \quad (13a)$$

These times are small

$R_p$ (cm)	0.1	0.01	0.001
$\tau_{gd}$ (s)	0.025	$2.5 \times 10^{-4}$	$2.5 \times 10^{-6}$
$\tau'_{gd}$ (s)	0.032	$3.2 \times 10^{-4}$	$3.2 \times 10^{-6}$

Characteristic gas diffusion time for particles (droplets) encountered in the atmosphere is very small O ( $10^{-3}$  s) or less.

## 9.1 Characteristic Equilibration Time at the Interface

We consider a droplet that initially contains no  $A$  exposed to air with concentration of  $A$ ,  $C_\infty$ . To this corresponds the partial pressure of  $A$ ,  $p_\infty = C_\infty RT$ . At equilibrium the liquid droplet concentration is  $C^* = H_A p_\infty = H_A RT C_\infty$ . We are interested in determining how fast  $C_i$  at the interface builds up from 0 to  $C^*$ .

Since from the point of view of molecules the interface is flat, we consider an element of the interface as a two-dimensional plane with no capacitance for molecules, i.e., no accumulation can occur at the interface. Then, the following balance must be established:

$$\begin{aligned} & (\text{arrival rate of gaseous A}) - (\text{return rate of A from interface}) = (\text{rate of diffusion of A into liquid}) \\ R_{-g} & \quad - \quad R_g \quad = \quad R_\ell \end{aligned} \quad (14)$$

$R_{-g} = (\text{No of molecules striking unit area per unit time}) \times (\text{accommodation coefficient})$

$$= \frac{1}{4} N \bar{u} \alpha = \frac{1}{4} \frac{P \alpha}{k_B T} \left( \frac{8 k_B T}{\pi m} \right) = \frac{\alpha P}{(2\pi k_B T m)^{1/2}} \quad (15)$$

The accommodation coefficient,  $\alpha$ , is the fraction of incoming molecules that get incorporated into the liquid. Hence, in molar units

$$R_{-g} = \frac{\alpha P}{(2\pi M RT)^{1/2}} \quad (16)$$

If the interface and gas were at equilibrium at some  $P_s$ , then, at those conditions  $R_{-g} \cong R_g$ .

This implies that the rate of "evaporation" is given by

$$R_g = \frac{\alpha P_s}{(2\pi M RT)^{1/2}} \quad (17)$$

where  $P_s$  is the interface partial pressure of  $A$  which is in equilibrium with  $C_s$ ,  $C_s = H_A P_s$ .

Hence,  $P_s$  can vary with time as  $C_s$  increases.

The flux into the liquid from the interface is given by

$$R_\ell = \frac{\alpha(P_\infty - P_s)}{(2\pi M RT)^{1/2}} = \frac{\alpha(C^* - C_s)}{H_A (2\pi M RT)^{1/2}} \quad (18)$$

Now consider Ficks Second Law for the liquid side of the interface

$$\frac{\partial C}{\partial t} = D_\ell \frac{\partial^2 C}{\partial x^2} \quad (19)$$

$$t = 0 \quad C = 0 \quad x \geq 0 \quad (20a)$$

$$x \rightarrow \infty \quad C \rightarrow 0 \quad t \geq 0 \quad (20b)$$

$$x = 0 \quad -D_\ell \frac{\partial C}{\partial x} = \frac{\alpha(C^* - C)}{H_A (2\pi M RT)^{1/2}} \quad (21)$$

Now there is no apparent characteristic dimension to scale with respect to. However, examination of units  $D_\ell$  ( $cm^2/s$ ) and  $\alpha/H_A (2\pi M RT)^{1/2}$  (cm/s) reveals a characteristic time scale of

$$\tau_p = \frac{D_\ell H_A^2 (2\pi M RT)}{\alpha^2} \quad (22)$$

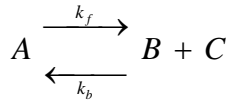
The solution indeed is given by:

$$C(x,t) = C^* \left\{ \operatorname{erfc} \left[ \frac{x}{2\sqrt{D_\ell t}} \right] - \exp \left( \frac{\kappa x}{D_\ell} \right) \exp \left( \frac{t}{\tau_p} \right) \operatorname{erfc} \left[ \left( \frac{t}{\tau_p} \right)^{1/2} + \frac{x}{2\sqrt{D_\ell t}} \right] \right\} \quad (23)$$

where  $\kappa = \alpha / H_A (2\pi M R T)^{1/2}$

As  $H_A \uparrow$   $\tau_p \uparrow$ ; as  $\alpha \downarrow$   $\tau_p \uparrow$   
 $M$   $H_A$   $\tau_p (s)$   
 $O_3$  48  $9.4 \times 10^{-3}$   $6.4 \times 10^{-15}$   
 $H_2O_2$  34  $7.1 \times 10^4$  0.26  
 $\tau_p$  is clearly very dependent on  $H_A$ .

## 9.2 Characteristic Time for Dissociation



We want to know how fast is equilibrium approached. At equilibrium

$$k_f [A]_e = k_b [B]_e [C]_e \quad (24)$$

Now define extent  $\xi$  and equilibrium extent  $\xi_e$

$$\begin{aligned} [A]_e &= [A_o] - \xi_e & [A] &= [A_o] - \xi \\ [B]_e &= [B_o] + \xi_e & [B] &= [B_o] + \xi \\ [C]_e &= [C_o] + \xi_e & [C] &= [C_o] + \xi \end{aligned} \quad (25)$$

and express all concentrations in terms of equilibrium ones:

$$\begin{aligned} [A] &= [A]_e - \Delta\xi \\ [B] &= [B]_e + \Delta\xi & \Delta\xi &= \xi - \xi_e \\ [C] &= [C]_e + \Delta\xi \end{aligned} \quad (26)$$

Now consider the rate of change of [A]

$$\frac{d[A]}{dt} = -k_f [A] + k_b [B][C] \quad (27)$$

$$-\frac{d\Delta\xi}{dt} = -k_f \{ [A]_e - \Delta\xi \} + k_b \{ [B]_e + \Delta\xi \} \{ [C]_e + \Delta\xi \} \quad (28)$$

Let:

$$\begin{aligned} \alpha &= k_f + k_b ([B]_e + [C]_e) \\ \beta &= k_b \end{aligned}$$

Then

$$\frac{d\Delta\xi}{dt} = -\alpha\Delta\xi - \beta\Delta\xi^2; \quad t = 0, \Delta\xi = \Delta\xi_0 \quad (29)$$

Solution of the above D.E. yields

$$\frac{\Delta\xi}{\Delta\xi_0} \frac{(\alpha + \beta\Delta\xi_0)}{(\alpha + \beta\Delta\xi)} = e^{-\alpha t} \quad (30)$$

Expressed in terms of [A] we get

$$\frac{[A] - [A]_e}{[A]_o - [A]_e} \left[ \frac{1 + \frac{\beta}{\alpha} ([A]_e - [A]_o)}{1 + \frac{\beta}{\alpha} ([A]_e - [A])} \right] = e^{-\alpha t} \quad (31)$$

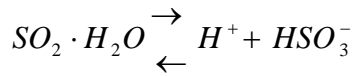
where

$$\frac{\beta}{\alpha} = \frac{1}{\frac{k_f}{k_b} + [B]_e + [C]_e} = \frac{1}{K + [B]_e + [C]_e} \quad (32)$$

If  $\frac{\beta}{\alpha} [A]_e \ll 1$ , then the characteristic time clearly is

$$\tau_i = \frac{1}{\alpha} = \frac{1}{k_f + k_b ([B]_e + [C]_e)} \quad (33)$$

For



at  $pH = 4$        $P_{SO_2} = 10^{-9} atm$

$$\frac{\beta[A]_e}{\alpha} = \frac{[SO_2 \cdot H_2O]_e}{K_{S_1} + [H^+]_e + [HSO_3^-]_e} = 10^{-2} \ll 1$$

$$\tau_i = \frac{1}{3.4 \times 10^6 + 2 \times 10^8 \left( [H^+]_e + [HSO_3^-]_e \right)} = 2 \times 10^{-7} s$$

Ionization equilibration is instantaneous.

### 9.3 Characteristic Time of Aqueous Diffusion

Consider diffusion in the droplet

$$\frac{\partial C}{\partial t} = \frac{D_\ell}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial C}{\partial r} \right) \quad (34)$$

$$t = 0 \quad C = 0 \quad (35a)$$

$$r = R_p \quad C = C_s \quad (35b)$$

$$r \rightarrow 0 \quad r \frac{\partial C}{\partial r} \rightarrow 0 \quad (36)$$

Scaling (dimensionalization) yields

$$\tau \propto \frac{R_p^2}{D_\ell} \quad (37)$$

Solution of the above is:

$$\frac{C(r,t)}{C_s} = 1 + \frac{R_p}{r} \sum_{n=1}^{\infty} (-1)^n \frac{2}{n\pi} \sin \left( \frac{n\pi r}{R_p} \right) e^{-\frac{n^2\pi^2 D_\ell t}{R_p^2}} \quad (38)$$

Traditionally, characteristic time is taken from the first exponential

$$\tau_{d\ell} = \frac{R_p^2}{\pi^2 D_\ell} \quad (39)$$

For  $D_\ell = 10^{-5} \text{ cm}^2\text{s}^{-1}$

$R_p$ (cm)	0.1	0.01	0.001
$\tau_{d\ell}$	$10^2$	1	$10^{-2}$

The total amount absorbed from  $t = 0$  to  $t = t$  is:

$$M(t) = 4\pi R_p^2 D_\ell \int_0^t \left. \frac{\partial C}{\partial r} \right|_{R_p} dt = 8\pi R_p D_\ell C_s \int_0^t \sum_{n=1}^{\infty} e^{-\frac{n^2\pi^2 D_\ell t}{R_p^2}} dt$$

$$M(t) = \frac{8R_p^3 C_s}{\pi} \left( \sum_{n=1}^{\infty} \frac{1}{n^2} - \sum_{n=1}^{\infty} \frac{1}{n^2} e^{-\frac{n^2\pi^2 D_\ell t}{R_p^2}} \right) \quad (40)$$

Since  $\sum_{n=1}^{\infty} \frac{1}{n^2} = \frac{\pi^2}{6}$

$$M_{\infty} = M(t \rightarrow \infty) = \frac{4\pi R_p^3 C_s}{3} \quad (41)$$

and

$$\frac{M(t)}{M_{\infty}} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} e^{-\frac{n^2 \pi^2 D_e t}{R_p^2}} \quad (42)$$

#### 9.4 Characteristic Reaction Time

$$\tau_{r\ell} = \frac{C_o}{R_o} \quad (43)$$

For example, for  $S(IV)$  oxidation

$$\tau_{r\ell} = \frac{[S(IV)]}{-R_{S(IV)}} \quad (44)$$

Based on gas phase concentrations this becomes

$$\tau_{rg} = \frac{[SO_2(g)]}{-R_{S(IV)}} = \frac{\tau_{r\ell}}{H_{SO_2}^* RT} \quad (45)$$

#### 9.5 Comparison of Characteristic Times

We have identified the following characteristic times:  $\tau_{dg}$ ,  $\tau_p$ ,  $\tau_i$ ,  $\tau_{d\ell}$ ,  $\tau_{r\ell}$  or  $\tau_{rg}$ . The summary of the defining expressions is in Table 1.

We have already stated that  $\tau_i$  is negligible i.e ionization reactions are always in equilibrium.

When  $\tau_{d\ell} \ll \tau_{r\ell}$ , the whole droplet reacts at a uniform concentration.

When  $\tau_{d\ell} \approx \tau_{r\ell}$  diffusion and reaction occur simultaneously, and both have to be considered.

When  $\tau_{d\ell} \gg \tau_{r\ell}$  reaction is diffusion limited.

When  $\tau_{dg} \ll \tau_{rg}$  the gas concentration profile has time to relax, and the surface of the drop can be assumed to be exposed to the bulk gas concentration.

When  $\tau_p \ll \tau_{r\ell}$  Henry's Law holds at the interface.



**TABLE 1: Comparison of characteristic times for aqueous-phase S(IV) Oxidation**

We have developed the following expressions for the characteristic times associated with aqueous-phase chemical reaction droplets:

1. Characteristic time for gas-phase diffusion

$$\tau_{dg} = \frac{R_p^2}{4D_g}$$

2. Characteristic time to achieve interfacial phase equilibrium

$$\tau_p = \frac{2\pi MRT D_1 H^2}{\alpha^2}$$

3. Characteristic time of aqueous dissociation reactions

$$A \xrightleftharpoons[k_r]{k_f} B + C$$
$$\tau_i = [k_f + k_r ([B]_e + [C]_e)]^{-1}$$

4. Characteristic time for aqueous-phase diffusion

$$\tau_{td} = \tau_{da} = \frac{R_p^2}{\pi^2 D_1}$$

5. Characteristic time for aqueous-phase chemical reaction

$$\tau_{r\ell} = \tau_{ra} = \frac{[S(IV)]}{d[S(IV)]/dt}$$
$$\tau_{rg} = -\frac{[SO_2(g)]}{d[S(IV)]/dt}$$

One can define the following criteria for droplet saturation with reactant gas at steady state:

$$\tau_p \leq 0.1 \tau_{r\ell} \quad \text{or}$$

1.  $\frac{2\pi MRT D_\ell H_A^2}{\alpha^2} \leq 0.1 \frac{1}{k}$

$$\tau_{d\ell} \leq 0.1 \tau_{r\ell}$$

2.  $\frac{R_p^2}{\pi D_\ell} \leq 0.1 \frac{1}{k}$

$$\tau_{dg} \leq 0.1 \tau_{rg}$$

3.  $\frac{R_p^2}{4D_g} \leq 0.1 \frac{1}{H_A kRT}$

All of these can be plotted on the log-log plots of  $H$  (or  $H^*$ ) vs  $k$

1.  $\log \left[ \frac{2\pi MRT D_\ell}{\alpha^2} \right] + 2 \log H_A \leq \log 10 - \log k$
2.  $\log \left[ \frac{R_p^2}{\pi D_\ell} \right] \leq -\log 10 - \log k$
3.  $\log \left[ \frac{R_p^2}{4D_g} \right] \leq -\log 10 - \log H_A RT - \log k$

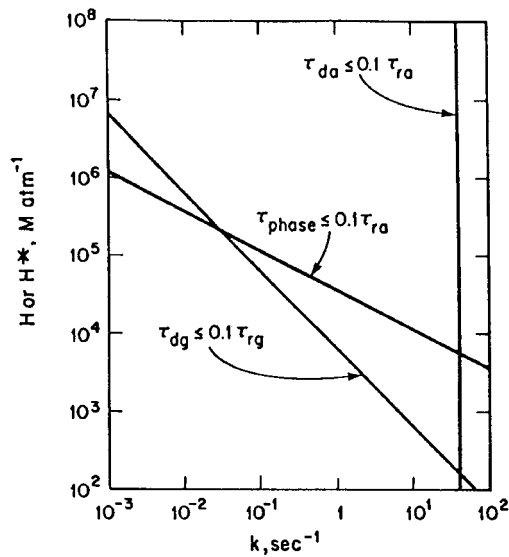
See Figure 1. The lines calculated are for  $D_\ell = 10^{-5}$  (cm<sup>2</sup>/s),  $D_g = 0.1$  (cm<sup>2</sup>/s),  $\alpha = 1$ ,  $2R_p = 10^{-3}$  cm.

1.  $H_A \leq 2.57 \times 10^5 M^{-1/2} k^{-1/2}$
2.  $k \leq 39.5 s^{-1}$
3.  $H_A \leq 6.55 \times 10^3 k^{-1}$

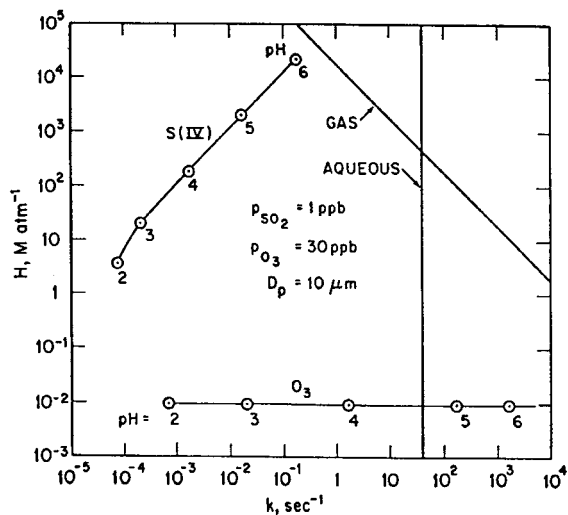
Figure 2 illustrates mass transfer limitation region for  $O_3$  oxidation of  $S(IV)$  at  $P_{O_3} = 3 \times 10^{-8}$  atm and  $P_{SO_2} = 10^{-9}$  atm.

Figure 3 indicates that both  $H_2O_2$  and  $SO_2$  liquid phase diffusion affect the  $H_2O_2$  oxidation rate of  $SO_2$  at pH < 2.

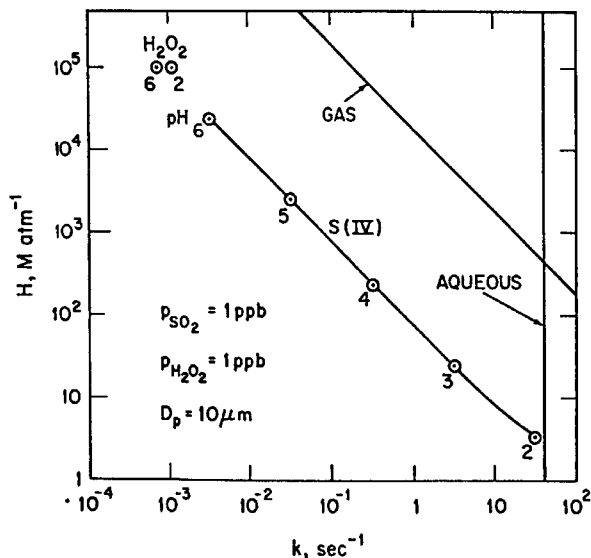
**FIGURE 1:** Bounds for mass transport limitation as a function of Henry's Law constant  $H$  or  $H^*$  and first-order rate constant for solution-phase reaction,  $k$ . Regions to the left and/or below each line represent combinations where mass transport is not limiting (Schwartz, 1984).



**FIGURE 2:** Mass transport limitations in the aqueous-phase  $S(IV) - O_3$  reaction. Gas and aqueous-phase bounds derived from Figure 1. The  $S(IV)$  curve is evaluated for  $p_{O_3} = 30 \text{ ppb}$ ; the  $O_3$  curve is evaluated for  $p_{SO_2} = 1 \text{ ppb}$ . The values of pH along each curve are indicated by the points. Values of  $k$  scale linearly with the partial pressure of the other reagent. Mass transport limitation is absent for points below and/or to the left of the lines (Schwartz, 1984).



**FIGURE 3:** Mass transport limitations in the aqueous-phase  $S(IV) - H_2O_2$  reaction. Gas and aqueous-phase bounds derived from Figure 1. The  $S(IV)$  curve is evaluated for  $p_{H_2O_2} = 1 \text{ ppb}$ ; the  $H_2O_2$  points are evaluated for  $p_{SO_2} = 1 \text{ ppb}$ . The values of pH are indicated by the points. Values of  $k$  scale linearly with the partial pressure of the other reagent. Mass transport limitation is absent for points below and/or to the left of the lines (Schwartz, 1984).



## 9.6 Diffusion to Falling Droplets

For stationary droplet external transport of gas at steady state yields

$$Sh = \frac{k_m 2R_p}{D_g} = 2 \quad (46)$$

where

$$J = -D_g \frac{dC}{dr} \Big|_{R_p} = k_m (C_\infty - C \Big|_{R_p}) \quad (47)$$

Hence,  $k_m = \frac{D_g}{R_p}$  results from the steady state analytical solution.

For moving droplets correlations are used of the form

$$Sh = 2 + 0.6 Re^{1/2} Sc^{1/3}$$

$$Re = \frac{v_t 2R_p}{\nu_{air}} \quad ; \quad v_t = \text{terminal droplet velocity}$$

$$\nu_{air} = \text{air kinematic viscosity} = \mu_{air} / \rho_{air}$$

$$Sc = \frac{\nu_{air}}{D_g}$$

If drops were rigid for  $R_p \geq 0.1 \text{ cm}$   $\tau_{d\ell}$  would be the limiting resistance. However, all droplets larger than  $R_p > 0.01 \text{ cm}$  develop internal circulation, the time scale of which is  $R_p \mu_\ell / \nu_t \mu_{air}$ . For a 0.1 cm droplet this is  $10^{-2} \text{ s}$  so that we can assume all drops larger than 0.01 cm to be well mixed.