

### S1 Simultaneous diffusion of NO<sub>2</sub>/N<sub>2</sub>O<sub>4</sub> in the TT experiment

After a short time, a time independent concentration profile is established in the diffusion capillaries of the TT experiment. The flows of the diffusing species are given by

$$J(\text{NO}_2) = D(\text{NO}_2) \left( \frac{\partial c(\text{NO}_2)}{\partial z} \right)_t, \quad (\text{S1})$$

$$J(\text{N}_2\text{O}_4) = D(\text{N}_2\text{O}_4) \left( \frac{\partial c(\text{N}_2\text{O}_4)}{\partial z} \right)_t. \quad (\text{S2})$$

It is assumed that the equilibrium between NO<sub>2</sub> and N<sub>2</sub>O<sub>4</sub> is established everywhere in the capillary. The equilibrium is described by Eq. (21). The total flux of the pseudo species N<sub>IV</sub> = NO<sub>2</sub> + 2 N<sub>2</sub>O<sub>4</sub> though the capillaries is given by

$$\begin{aligned} J(\text{N}_{\text{IV}}) &= J(\text{NO}_2) + 2J(\text{N}_2\text{O}_4), \\ &= D(\text{NO}_2) \left( \frac{\partial c(\text{NO}_2)}{\partial z} \right)_t \\ &\quad + 2D(\text{N}_2\text{O}_4) \left( \frac{\partial c(\text{N}_2\text{O}_4)}{\partial z} \right)_t \end{aligned}$$

The concentration gradients of NO<sub>2</sub> and N<sub>2</sub>O<sub>4</sub> are not independent. They are joined by Eq. (21):

$$\left( \frac{\partial c(\text{N}_2\text{O}_4)}{\partial z} \right)_t = \frac{2RTc(\text{NO}_2)}{p^\ominus K} \left( \frac{\partial c(\text{NO}_2)}{\partial z} \right)_t \quad (\text{S3})$$

Therefore, it is obtained setting  $c = c(\text{NO}_2)$

$$J(\text{N}_{\text{IV}}) = \left( \frac{\partial c}{\partial z} \right)_t \left[ D(\text{NO}_2) + c \frac{4RTD(\text{N}_2\text{O}_4)}{p^\ominus K} \right]. \quad (\text{S4})$$

This differential equation describes the concentration of NO<sub>2</sub> as function of the capillary coordinate  $z$ . This equation easily can be solved because due to mass conservation  $J(\text{N}_{\text{IV}})$  is independent of  $z$ . It is obtained after rearrangement

$$\int_{c_1}^{c_2} \left[ D(\text{NO}_2) + c \frac{4RTD(\text{N}_2\text{O}_4)}{p^\ominus K} \right] dc = \int_0^l J(\text{N}_{\text{IV}}) dz. \quad (\text{S5})$$

It is assumed as boundary condition that the concentration at the low concentration side is approximately 0. After integration this equation is written as

$$J(\text{N}_{\text{IV}})l = D_{\text{NO}_2}c(\text{NO}_2) + \frac{2RTD(\text{N}_2\text{O}_4)c^2(\text{NO}_2)}{p^\ominus K} \quad (\text{S6})$$

After back substitution of Eq. (21) this yields Eq. (19) which is the same result one would obtain if NO<sub>2</sub> and N<sub>2</sub>O<sub>4</sub> are not coupled by equilibrium and would diffuse independently.

For further discussion, the degree of dissociation  $\alpha$  is defined by Eq. (20). Therefore, Eq. (19) is written as

$$J(\text{N}_{\text{IV}}) = D(\text{N}_{\text{IV}}) \frac{c(\text{N}_{\text{IV}})}{l} \quad (\text{S7})$$

using

$$D(\text{N}_{\text{IV}}) = \alpha D(\text{NO}_2) + (1 - \alpha) D(\text{N}_2\text{O}_4) \quad (\text{S8})$$

$\alpha$  is obtained from Eq. (21):

$$\alpha = \frac{Kp^\ominus}{4p(\text{N}_{\text{IV}})} \left( \sqrt{1 + \frac{8p(\text{N}_{\text{IV}})}{Kp^\ominus}} - 1 \right). \quad (\text{S9})$$

$p(\text{N}_{\text{IV}})$  corresponds to the NO<sub>2</sub> partial pressure at room temperature in the high concentration flow tube.

### S2 Nomenclature

$b$	temperature coefficient of diffusion
$c$	concentration
$D$	diffusion coefficient
$D_0$	diffusion coefficient at STP
$J$	flux
$k$	Boltzmann constant
$k_1$	first order loss rate
$K$	equilibrium constant
$l$	length of diffusion capillary
$m$	molecular mass
$M$	molar mass
$n$	number of capillaries in the TT experiment
$\dot{n}$	carrier gas mass flow rate
$p$	pressure
$p_0$	pressure at normal conditions ( $1.013 \times 10^5$ Pa)
$p^\ominus$	standard pressure ( $10^5$ Pa, IUPAC)
$P$	probability value
$r$	column radius
$R$	gas constant
$t$	time
$t_a$	arrest time of AF method
$T$	temperature
$T_0$	273.15 K
$v$	carrier gas velocity
$V$	atomic volume increment
$\dot{V}$	volume flow rate
$x$	mole fraction
$z$	coordinate of column or capillary axis
$\alpha$	degree of dissociation
$\epsilon$	characteristic energy of Lennard-Jones potential
$\eta$	viscosity
$\Theta$	reduced temperature
$\Omega_D$	dimensionless collision integral for diffusion
$\sigma$	characteristic length of Lennard-Jones potential
$\varsigma_t^2$	peak variance of the AF method (units of time)
$\varsigma_z^2$	peak variance of the AF method (units of length)