Supplement of

Timescales of Secondary Organic Aerosols to Reach Equilibrium at Various Temperatures and Relative Humidities

Ying Li¹, and Manabu Shiraiwa¹,*

[1] Department of Chemistry, University of California, Irvine, California, USA.

*Correspondence to: Manabu Shiraiwa (m.shiraiwa@uci.edu)
Table S1. Temperature-dependent kinetic parameters used in the simulations.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
<th>Equation$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\omega$ (cm s$^{-1}$)</td>
<td>mean thermal velocity</td>
<td>$\omega (T) = (8RT/(\pi M))^{1/2}$</td>
</tr>
<tr>
<td>$D_g$ (cm$^2$ s$^{-1}$)</td>
<td>gas-phase diffusion coefficient</td>
<td>$D_g(T, P) = (T/T_{\text{standard}})^{1.75} (P_{\text{standard}}/P) D_g$ (T_{\text{standard}}, P_{\text{standard}}) \text{ }^b$</td>
</tr>
<tr>
<td>$D_b$ (cm$^2$ s$^{-1}$)</td>
<td>bulk diffusion coefficient</td>
<td>$D_b(T, RH) = kT/(6\pi a\eta(T, RH))$</td>
</tr>
<tr>
<td>$k_a$ (cm s$^{-1}$)</td>
<td>first-order adsorption rate coefficient</td>
<td>$k_a(T) = \alpha_s \omega(T)/4$</td>
</tr>
<tr>
<td>$k_d$ (s$^{-1}$)</td>
<td>first-order desorption rate coefficient</td>
<td>$k_d(T) = Ae^{-(E_{\text{des}}/(RT))}$</td>
</tr>
<tr>
<td>$k_{ss,s}$ (cm s$^{-1}$)</td>
<td>first-order rate coefficient for quasi-static-to-sorption layer transport</td>
<td>$k_{ss,s}(T, RH) = 2D_b(T, RH)/(\delta_{ss} + \delta_Z)$</td>
</tr>
<tr>
<td>$k_{ss}$ (s$^{-1}$)</td>
<td>first-order rate coefficient for sorption-to-quasi-static surface transport</td>
<td>$k_{ss}(T, RH) = k_{ss,s}(T, RH)k_d(T)[Z]<em>{ss,eq}/(k_a(T)[Z]</em>{g,eq})$</td>
</tr>
<tr>
<td>$k_{b1,ss}$ (cm s$^{-1}$)</td>
<td>rate coefficient of bulk layer 1-to-quasi-static surface transport</td>
<td>$k_{b1,ss}(T, RH) = 2D_b(T, RH)/(\delta_{ss} + \delta(1))$</td>
</tr>
<tr>
<td>$k_{ss,b1}$ (cm s$^{-1}$)</td>
<td>rate coefficient of surface-to-bulk layer 1 transport</td>
<td>$k_{ss,b1}(T, RH) = k_{b1,ss}(T, RH)$</td>
</tr>
<tr>
<td>$k_b$ (cm s$^{-1}$)</td>
<td>rate coefficient of transport between bulk layers</td>
<td>$k_b(T, RH) = 2D_b(T, RH)/(\delta(k) + \delta(k + 1))$</td>
</tr>
<tr>
<td>$\tau_d$ (s)</td>
<td>desorption lifetime</td>
<td>$\tau_d = k_d^{-1}$</td>
</tr>
</tbody>
</table>

$^a$ Description and the values of the symbols shown in the equations are summarized in Table S2.

$^b$ $D_g(T_{\text{standard}}, P_{\text{standard}})$ is calculated by the EPA on-line tools: (https://www3.epa.gov/ceampubl/learn2model/part-two/onsite/estdiffusion-ext.html).
Table S2. Description and the values of the symbols in the equations of Table S1.

<table>
<thead>
<tr>
<th>Variable (Unit)</th>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R$ (J K$^{-1}$ mol$^{-1}$)</td>
<td>gas constant</td>
<td>8.314</td>
</tr>
<tr>
<td>$T$ (K)</td>
<td>temperature</td>
<td>varied from 220 to 310</td>
</tr>
<tr>
<td>RH (%)</td>
<td>relative humidity</td>
<td>varied from 0 to 100</td>
</tr>
<tr>
<td>$M$ (g mol$^{-1}$)</td>
<td>molar mass of compound Z</td>
<td>200</td>
</tr>
<tr>
<td>$T_0$ (K)</td>
<td>room temperature</td>
<td>298</td>
</tr>
<tr>
<td>$\rho$ (g cm$^{-3}$)</td>
<td>density of organic particles</td>
<td>1.4</td>
</tr>
<tr>
<td>$T_{\text{standard}}$ (K)</td>
<td>sea level standard temperature</td>
<td>288.15</td>
</tr>
<tr>
<td>$P_{\text{standard}}$ (Pa)</td>
<td>sea level standard atmospheric pressure</td>
<td>101325</td>
</tr>
<tr>
<td>$K$ (J K$^{-1}$)</td>
<td>Boltzmann constant</td>
<td>$1.38 \times 10^{-23}$</td>
</tr>
<tr>
<td>$a$ (cm)</td>
<td>effective molecular radius</td>
<td>$1 \times 10^{-8}$</td>
</tr>
<tr>
<td>$\delta_Z$ (cm)</td>
<td>effective molecular diameter</td>
<td>$2 \times 10^{-8}$</td>
</tr>
<tr>
<td>$\alpha_s$</td>
<td>surface accommodation coefficient on free-substrate</td>
<td>1</td>
</tr>
<tr>
<td>$A$ ($s^{-1}$)</td>
<td>pre-exponential factor</td>
<td>$10^{12}$</td>
</tr>
<tr>
<td>$E_{\text{des}}$ (kJ mol$^{-1}$)</td>
<td>desorption energy</td>
<td>40</td>
</tr>
<tr>
<td>$[Z]_{\text{g,eq}}$ (cm$^{-3}$)</td>
<td>equilibrium (saturation) number concentrations of Z in the gas phase</td>
<td>variable</td>
</tr>
<tr>
<td>$[Z]_{\text{ss,eq}}$ (cm$^{-2}$)</td>
<td>equilibrium (saturation) number concentrations of Z in the quasi-static surface layer</td>
<td>variable</td>
</tr>
<tr>
<td>$\delta_{ss}$ (cm)</td>
<td>thickness of the quasi-static surface layer</td>
<td>variable</td>
</tr>
<tr>
<td>$\delta(k)$ (cm)</td>
<td>thickness of the bulk layer $k$</td>
<td>variable</td>
</tr>
</tbody>
</table>
Figure S1. Temperature-dependent kinetic processes simulated in the KM-GAP model. Parameters in blue are treated as a function of temperature (Table S1). \([Z]\) are concentrations of species \(Z\) in the gas (g) and near-surface gas phases (gs), at the sorption layer (s) and in the surface (ss) and in the bulk (b) layers. \(J\) are the transport fluxes between each layer, including the gas-phase diffusion flux \(J_{\text{diff}}\), the adsorption \(J_{\text{ads}}\) and desorption \(J_{\text{des}}\) fluxes, surface–bulk exchange fluxes \(J_{s,ss}, J_{ss,s}, J_{ss,b1}, J_{b1,ss}\), and bulk diffusion fluxes \(J_{b,b}\).

Figure S2. Bulk diffusion coefficient \((D_b)\) in pre-existing particles as a function of temperature and relative humidity. The glass transition temperatures under dry conditions \((T_{g,\text{org}})\) are set to be (a) 240 K, (b) 270 K and (c) 300 K, respectively.
Figure S3. Temporal evolution of the mass fraction of Z in the near-surface bulk ($f_s$), and the average fraction of Z in the entire bulk ($f_b$). RH = 60% and $T$ is (a, b) 298 K and (c, d) 250 K. The $C_0$ of Z is (a, c) 10 µg m$^{-3}$ and (b, d) 0.1 µg m$^{-3}$. The glass transition temperature of pre-existing particles under dry conditions ($T_{g,org}$) is set to be 270 K, which leads to $D_b$ of (a, b) $10^{-11}$ cm$^2$ s$^{-1}$ and (c, d) $10^{-18}$ cm$^2$ s$^{-1}$. The initial mass concentration of pre-existing particles is assumed to be 20 µg m$^{-3}$ with the number concentrations of $3 \times 10^4$ cm$^{-3}$ and the initial particle diameter of 100 nm.

Figure S4. Temporal evolution of mass concentrations of the condensing compound Z in the gas phase ($C_g$), just above the particle surface ($C_s$), and in the particle phase ($C_p$). The mass fraction of Z in the near-surface bulk ($f_s$), and the average fraction of Z in the entire particle bulk ($f_b$) are also shown. $D_b$ is $10^{-18}$ cm$^2$ s$^{-1}$. The $C_0$ of Z is (a) 0.1 µg m$^{-3}$ and (b) $10^{-9}$ µg m$^{-3}$. The initial mass concentration of pre-existing particles is set to be (a) 0.7 µg m$^{-3}$ and (b) 20 µg m$^{-3}$. $\tau_{eq}$ is marked with the red circle. $\tau_{eq}$ (~28 s) in (b) is consistent with the inverse of the condensation sink (29 s).
Figure S5. Temporal evolution of mass concentrations of the condensing compound Z in the gas phase ($C_g$), just above particle surface ($C_s$), in the particle phase ($C_p$), the mass fraction of Z in the near-surface bulk ($f_s$), and the average fraction of Z in the entire particle bulk ($f_b$). $\tau_{eq}$ are marked with red circles. RH = 60% and $T$ is (a–b) 298 K and (c–d) 250 K. The $C_0$ of the condensing compound is (a, c) 10 µg m$^{-3}$ and (b, d) 0.1 µg m$^{-3}$. The glass transition temperature of pre-existing particles under dry conditions ($T_{g,org}$) is set to be 270 K, which leads to $D_b$ of (a, b) $10^{-11}$ cm$^2$ s$^{-1}$ and (c, d) $10^{-18}$ cm$^2$ s$^{-1}$. The initial mass concentration of pre-existing non-volatile particles ($C_{OA}$) is assumed to be 20 µg m$^{-3}$ with the number concentrations of $3 \times 10^8$ cm$^{-3}$ and the initial particle diameter of 100 nm.