Supporting Information: Nanoparticle Growth by Particle Phase Chemistry

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Three figures (S1-S3) and associated discussion.

Figure S1

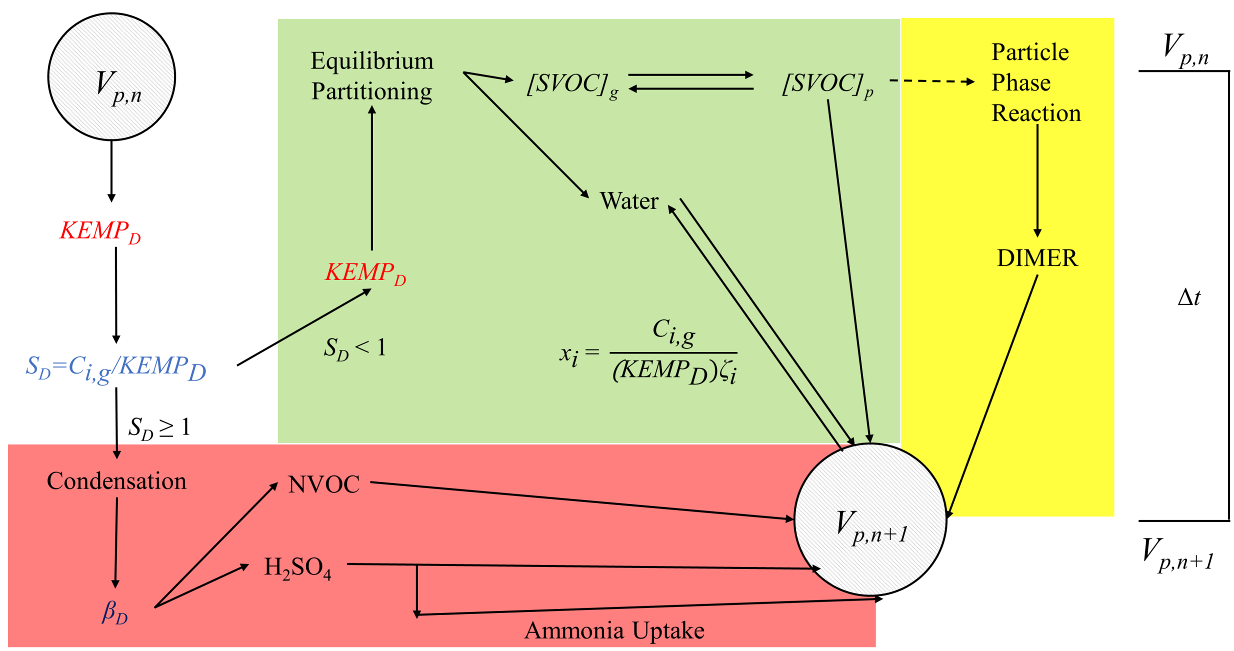


Figure S1 shows a schematic of the iterative calculations, starting with volume $V_{p,n}$, the total volume of the particle at the start of time period *n*. Calculations begin with the Kelvin modified vapor pressure ($KEMP_D$) given as:

(S1) $KEMP_D = P_0 e^{\left[(2\sigma V_{M,p})/\left(\frac{D}{2}RT\right)\right]}$,

where P_0 is the saturation vapor pressure over a flat surface, σ is the surface tension, $V_{M,p}$ is the average molar volume of the particle, *D* is the particle diameter, *R* is the universal gas constant, and *T* is the temperature. Subscript *D* shown here with $KEMP_D$, and for other variables hereafter, denotes the size dependence of the term. $KEMP_D$ defines the saturation ratio (S_D), which determines whether uptake will occur at a rate either equal to or less than the condensation rate. The saturation ratio is

(S2) $S_D = C_{i,g}/KEMP_D$.

For compounds having $S_D < 1$, uptake occurs at a slower rate than the condensation rate, while for compounds having $S_D >> 1$, uptake occurs at the condensation rate.

For the molecular species considered in this study, those growing the particle at the condensation rate (green shaded region) are sulfuric acid and non-volatile organic compound (NVOC). Equation 1 in the main text gives the uptake rate, which assumes that every collision results in uptake. The Fuchs-Sutugin mass transfer correction factor β_D is given by:

(S3) $$\beta_D = \frac{1+Kn}{1+\left((4/3\alpha)+0.337\right)(Kn)+(4/3\alpha)(Kn)^2}$$

where α is the mass accommodation coefficient (assumed to be 1) and Kn is the Knudsen number:

(S4) $$Kn = \frac{2\lambda}{D},$$

where λ is the mean free path and D is particle diameter. The mean free path is defined as:

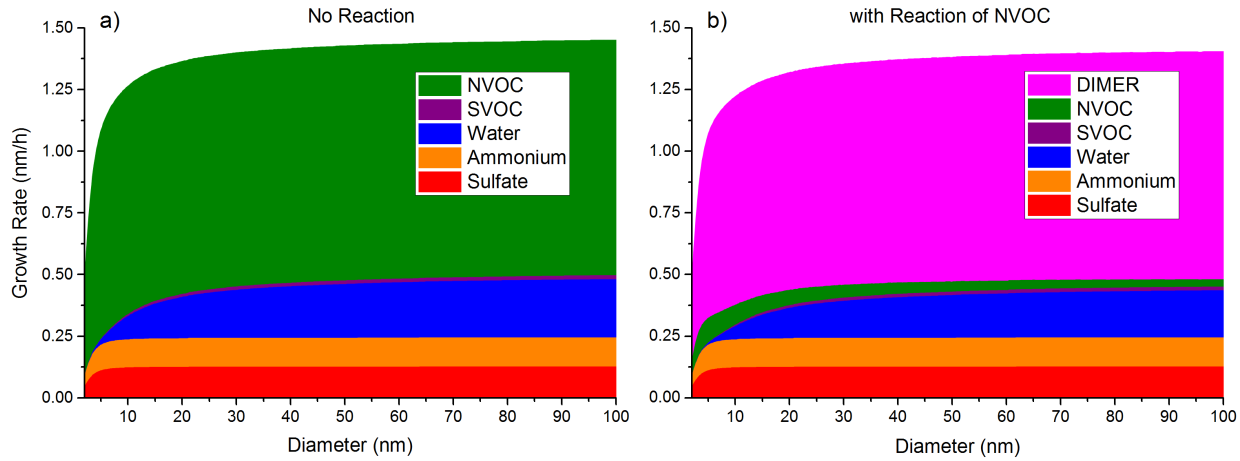
(S5) $$\lambda = \frac{k_B T}{\sqrt{2} P \pi \left((D+D_i)/2 \right)^2}$$

where k_B is the Boltzmann constant, T is the temperature, P is the atmospheric pressure, and D_i is the diameter of a gas molecule i.

Semi-volatile organic compounds (SVOC) cause particle growth at a rate that is slower than the condensation rate (yellow shaded region). Based on the gas phase mixing ratio and particle properties, a corresponding equilibrium particle phase concentration is calculated (Eq. 2 of the main text). The mass of such species added to the particle is based on $V_{p,n}$, so by $V_{p,n+1}$, the species is no longer in equilibrium and must be re-calculated. Partitioning of water is dependent on the mixing ratio and the $KEMP_D$ to determine the equilibrium mole fraction x_i. For simplicity, the activity coefficient (ζ) is assumed to be 1.

Particle phase chemistry occurs by an accretion reaction (red shaded region). Reactions are modeled by the second order decay of SVOC (or in the case of Figures S2 and S3, NVOC) to produce DIMER products. Depletion of SVOC is dependent on the concentration of SVOC existing in the particle at $V_{p,n}$. When equilibrium is re-calculated for SVOC at $V_{p,n+1}$, the mass added to the particle must account for both depletion by reaction and dilution due to particle growth. When the volume changes for all individual species have been calculated, they are summed to give the new particle volume, $V_{p,n+1}$. After volume $V_{p,n+1}$ is achieved, calculations are iteratively repeated.

Figure S2



Figures S2a and b show the size dependent evolution of particle growth rate by a) partitioning alone and b) with dimer formation from NVOC ($k_{II} = 10^{-3}$ $M^{-1}s^{-1}$). Dimer formation from NVOC does not enhance the growth rate (growth still proceeds at the NVOC collision rate), but it does change the composition.

Figure S3

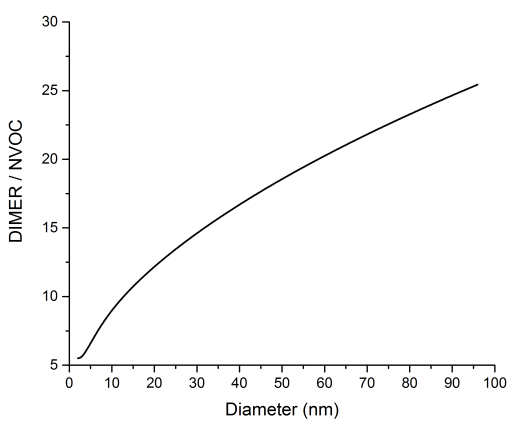


Figure S3 shows the mass fraction ratio of DIMER to NVOC, which increases systematically with increasing particle diameter.