

**FIGURE 14.15** Increased condensation with increasing quantities of  $\alpha$ -pinene + ozone products, with the shaded portion of each bar showing the condensed-phase material and the remainder showing the material in the vapor phase: (a) partitioning when a relatively low concentration of  $\alpha$ -pinene is oxidized, resulting in  $1 \mu\text{g m}^{-3}$  of SOA mass or a fraction of SOA produced to  $\alpha$ -pinene consumed (the SOA yield) of 0.04; (b) partitioning with 18 times as much precursor, resulting in 100 times as much SOA and a SOA yield of 0.21. Note that the bin with 50:50 partitioning shifts to  $100 \mu\text{g m}^{-3}$ . (Source: Donahue, N. M., et al., *Atmos. Environ.* **43**, 94–106 (2009), Figure 1.)

### Example: Partitioning in the VBS

To illustrate the process, let us consider SOA formation in the  $\alpha$ -pinene +  $O_3$  system. Let us assume that  $25 \mu\text{g m}^{-3}$  of  $\alpha$ -pinene is reacted and that for each  $1 \mu\text{g m}^{-3}$  reacted,  $1.47 \mu\text{g m}^{-3}$  of products result; this accounts for the mass increase owing to addition of oxygen. (The value is slightly different than the 1.4 used in Figures 14.13 and 14.14.) It is necessary to specify the fraction of the mass of reaction products in each volatility class to the total mass of 1.47. Say that this distribution is as follows:

$C^*$	0.01	0.1	1.0	10	100	$10^3$	$10^4$	$10^5$	$10^6$
Mass fraction	0.004	0.002	0.05	0.09	0.12	0.18	0.4	0.35	0.27

The mass fractions add up to 1.47. Now, begin at the  $0.01 \mu\text{g m}^{-3}$  bin. The mass of products in this bin is  $0.004 \times 25 = 0.1 \mu\text{g m}^{-3}$ . The fraction of that product in the particle phase is computed using (14.43). With  $C^* = 0.01$  and  $C_{OA} = 0.1$ ,  $X_p = 1/1.1 = 0.91$ , which we say is  $\sim 1.0$ . Now move to the 0.1 bin. The mass in the 0.1 bin is  $0.002 \times 25 = 0.05 \mu\text{g m}^{-3}$ . In calculating the fraction of OA in that bin, we have to consider the OA from both the 0.01 and 0.1 bins. This total is taken as  $0.1 + 0.05 = 0.15$ , where, for the moment, we put all the mass from the 0.1 bin into OA. Then, for the 0.1 bin,  $C^*/C_{OA} = 0.1/0.15$ , and  $X_p = 0.6$ . Let's call that 1.0. Now go to the 1.0 bin. The mass of products is  $0.05 \times 25 = 1.25 \mu\text{g m}^{-3}$ . Since we know that we are getting close to the 50/50 point in the  $X_p$  curve, let us arbitrarily put half of this product,  $0.625 \mu\text{g m}^{-3}$ , into this bin. Doing so, the  $C^*/C_{OA} = 1.0/0.775$  and  $X_p = 0.44$ , which is close enough to 0.5, so our assumption of putting half the mass into the OA phase was a good one. If we proceed to the  $10 \mu\text{g m}^{-3}$  bin, the mass of products =  $2.25 \mu\text{g m}^{-3}$ . It would seem reasonable to assume that one-tenth of this will partition into the particle phase, so

we add  $0.225 \mu\text{g m}^{-3}$  to the accumulated  $C_{\text{OA}}$ , giving a total of  $1.0 \mu\text{g m}^{-3}$ . This results in  $X_p = 1/11$  for this bin, which is sufficiently close to 0.1. For the  $100 \mu\text{g m}^{-3}$  bin, the product is  $0.12 \times 25 = 3.0 \mu\text{g m}^{-3}$ . If we place 0.01 of this into the OA, then the total OA up to this bin = 1.03, and  $X_p \sim 0.01$ . From this bin on, we assume that the products remain entirely in the gas phase. With  $25 \mu\text{g m}^{-3}$  of  $\alpha$ -pinene reacted and a total of  $1.03 \mu\text{g m}^{-3}$  OA formed, the SOA yield =  $1.03/25 = 0.04$ .

What is the result if  $500 \mu\text{g m}^{-3}$  of  $\alpha$ -pinene is reacted? We can follow the same procedure of apportioning the oxidation products bin-by-bin. We find that the  $C_{\text{OA produced}} = 118 \mu\text{g m}^{-3}$  and the SOA yield =  $118/500 = 0.236$ . (This calculation is the subject of Problem 14.6 at the end of this chapter.) By increasing the initial VOC concentration 20-fold, we find that the SOA yield increases from 4% to 23.6%. This example highlights the fact that with a greater amount of VOC reacted, the ultimate SOA yield increases owing to the fact that the larger mass of SOA shifts the gas-particle partitioning of more volatile compounds toward the particle phase. In fact, most of the particle-phase SOA compounds at a mass loading of  $118 \mu\text{g m}^{-3}$  are not in the particle phase at a loading of  $1 \mu\text{g m}^{-3}$ .

In the calculations above, we started by assuming the distribution of volatilities of the oxidation products. Ordinarily, these will not be known a priori. It is necessary to make an initial guess, go through the bin-by-bin calculation, and then adjust the distribution by trial-and-error to fit the observed data. The curve in Figure 14.16 is a result of that process. Note that for the case in Figure 14.16 the SOA contained in the  $10^4$ ,  $10^5$ , and  $10^6$  bins, as indicated by the dark gray bars, had to be assumed to close the mass balance on SOA.

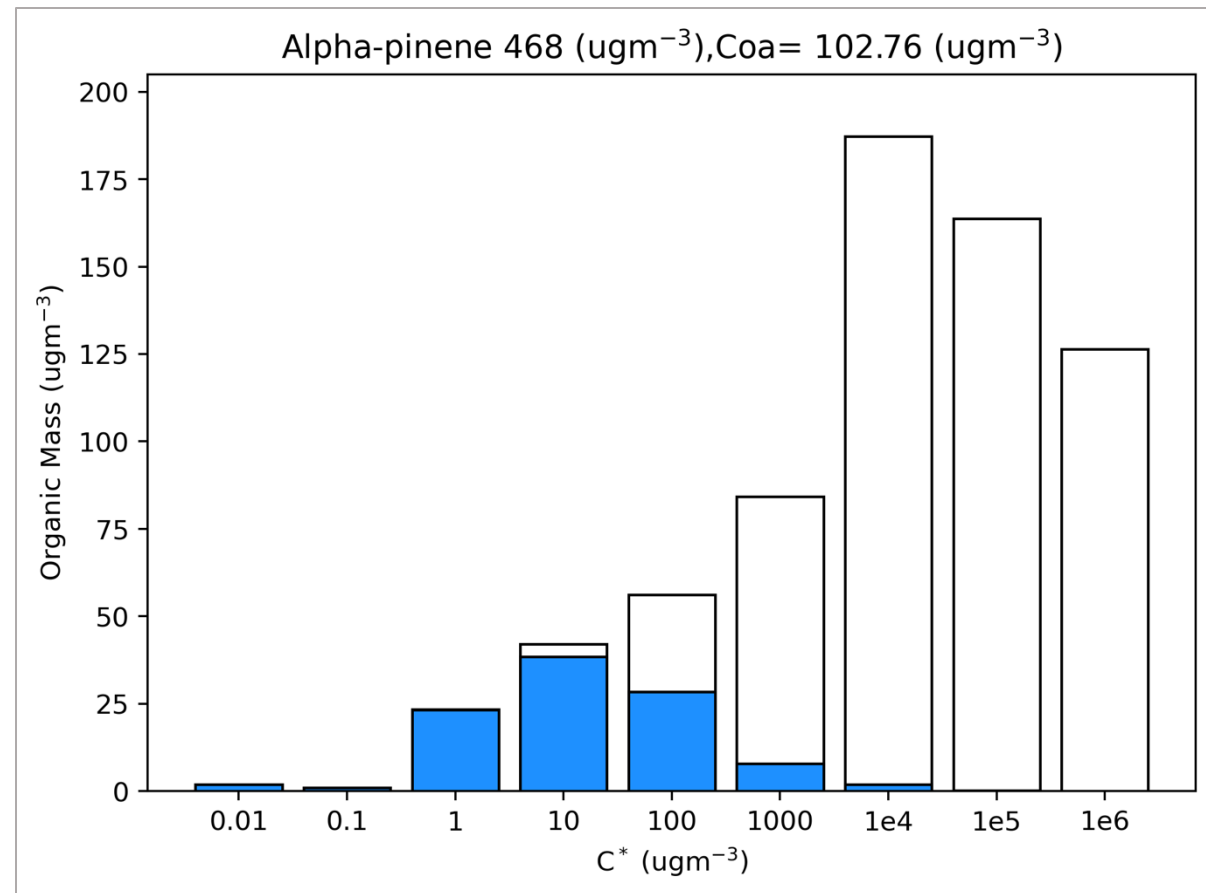
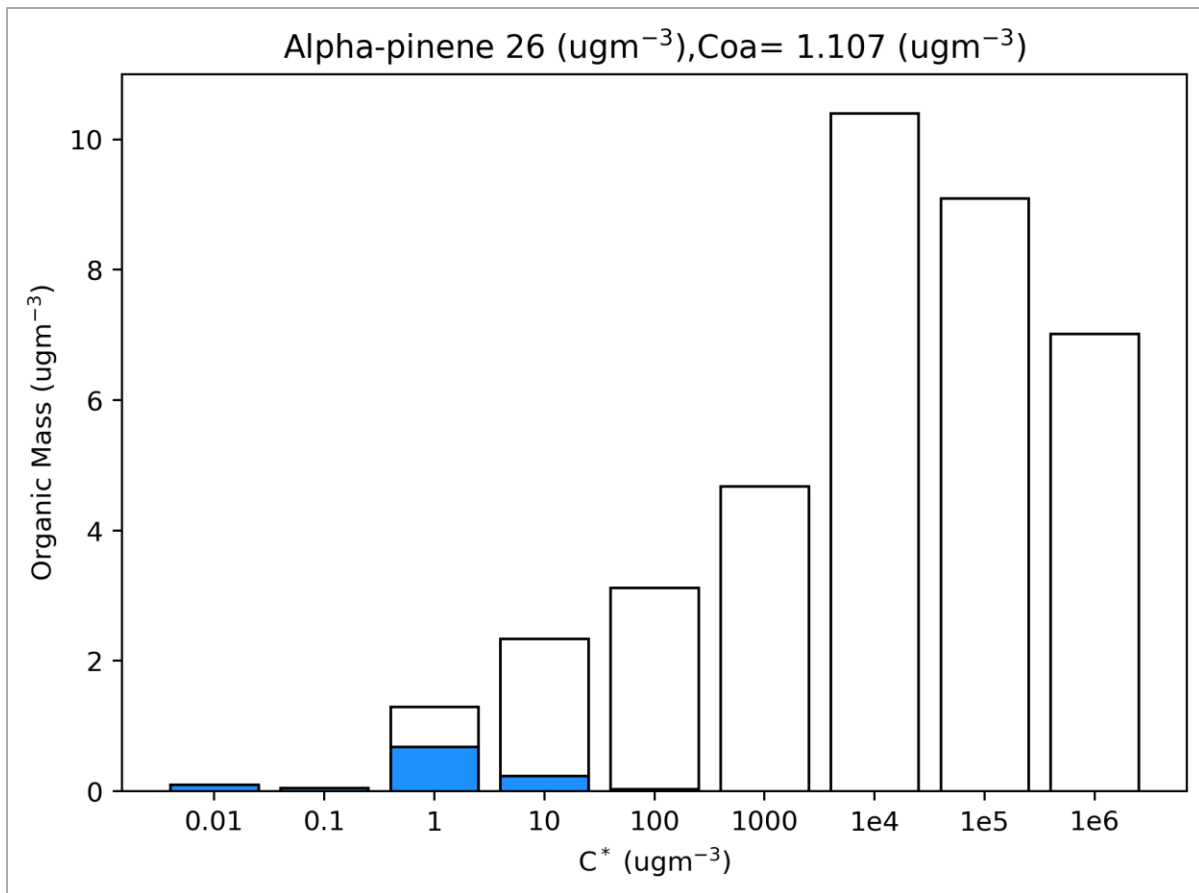
The VBS in SOA model. The enthalpy value is assumed.

```
In [50]: test.oaspc(['name', 'gas_name', 'ctr_name', 'alpha', 'cstar', 'enth'])
```

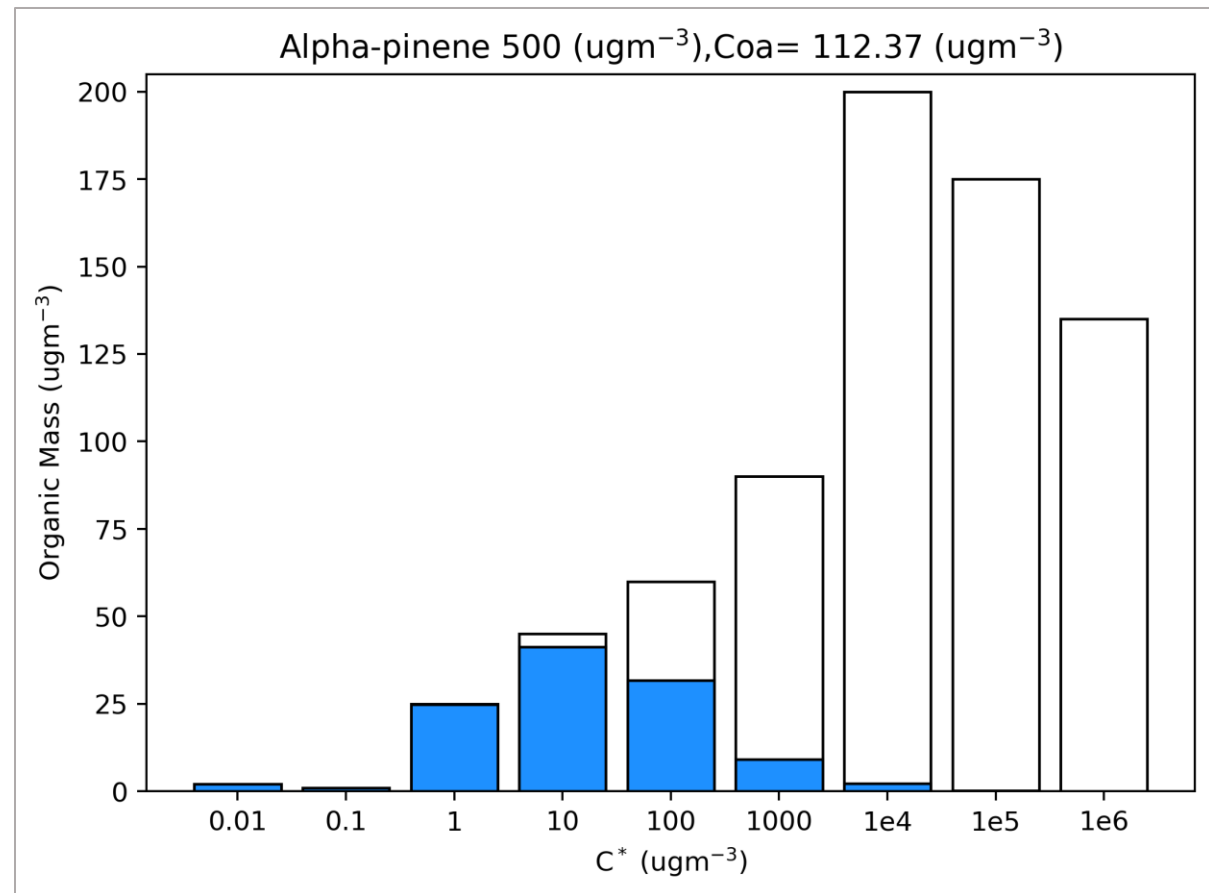
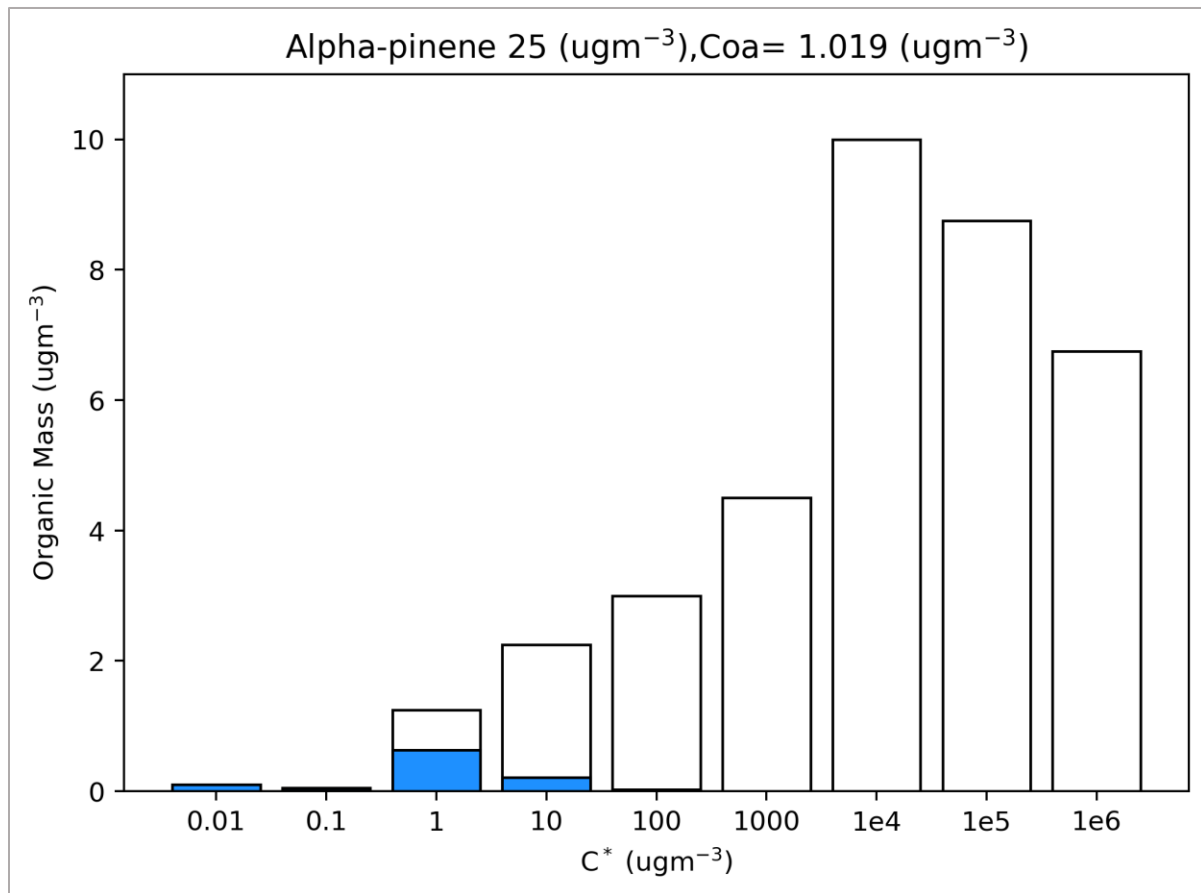
```
Out[50]:
```

	name	gas_name	ctr_name	alpha	cstar	enth
0	AAPIN1	SVAPIN1	APINRXN	0.004	0.01	102000
1	AAPIN2	SVAPIN2	APINRXN	0.002	0.10	102000
2	AAPIN3	SVAPIN3	APINRXN	0.050	1.00	102000
3	AAPIN4	SVAPIN4	APINRXN	0.090	10.00	102000
4	AAPIN5	SVAPIN5	APINRXN	0.120	100.00	102000
5	AAPIN6	SVAPIN6	APINRXN	0.180	1000.00	102000
6	AAPIN7	SVAPIN7	APINRXN	0.400	10000.00	102000
7	AAPIN8	SVAPIN8	APINRXN	0.350	100000.00	102000
8	AAPIN9	SVAPIN9	APINRXN	0.270	1000000.00	102000

## Output from SOA model



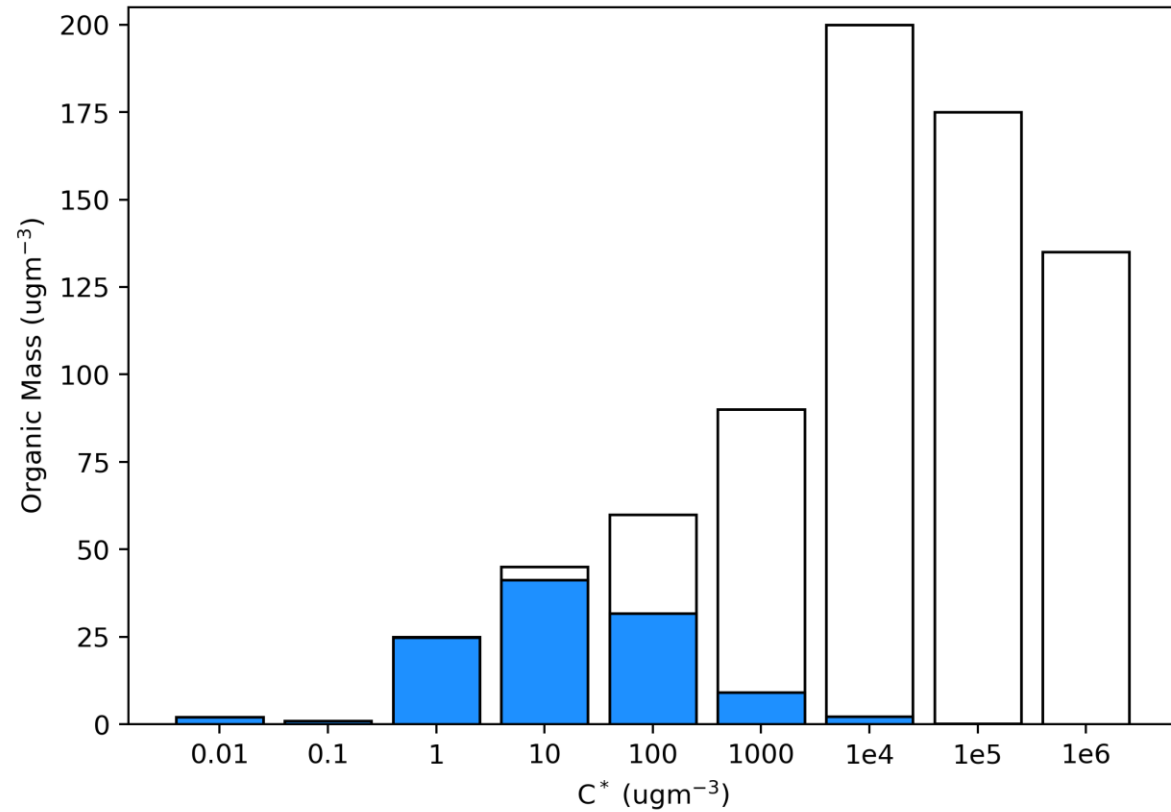
## Output from SOA model



## Output from SOA model: Temperature sensitivity test

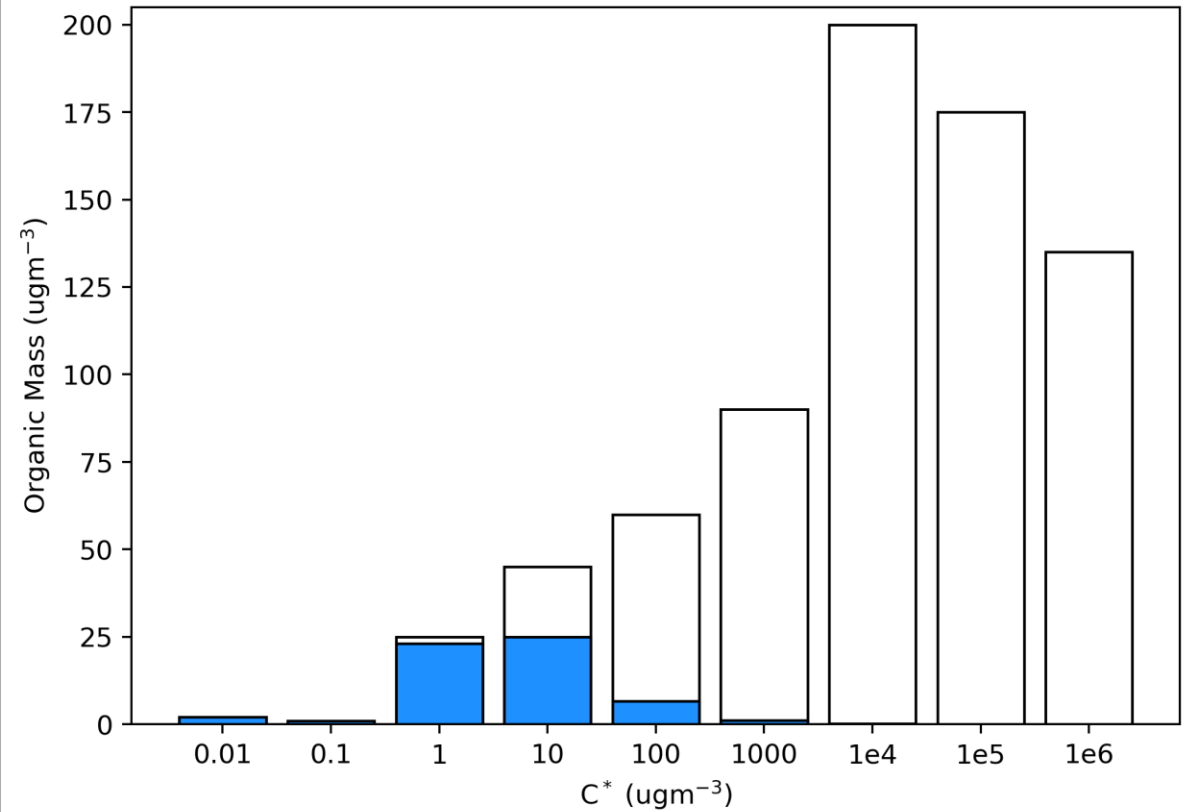
T= 298 K

Alpha-pinene 500 ( $\mu\text{g m}^{-3}$ ), Coa= 112.37 ( $\mu\text{g m}^{-3}$ )



T= 310 K

Alpha-pinene 500 ( $\mu\text{g m}^{-3}$ ), Coa= 59.21 ( $\mu\text{g m}^{-3}$ )

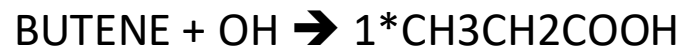




14.2<sub>A</sub> Assume that the gas-phase oxidation of 1-butene gives exclusively propionic acid ( $\text{CH}_3\text{CH}_2\text{COOH}$ ). At 298 K the vapor pressure of propionic acid is 0.005 atm.

- a. Assume that 100 ppb of 1-butene is reacted in the presence of  $100 \mu\text{g m}^{-3}$  of preexisting aerosol of molecular weight 100. Calculate the aerosol-phase concentration of propionic acid if it forms an ideal solution with the preexisting aerosol.

**Solution:**



$$\alpha = 1$$

$$P_o = 0.005 \text{ atm}$$

$$M_i = 74.08 \text{ g/mol}$$

$$M_{\text{voc}} = 56 \text{ g/mol}$$

$$\begin{aligned} C_{\text{tot}} &= \alpha * M_i / M_{\text{voc}} * \Delta(\text{VOC}) \\ &= 1 * 74.08 / 56 * 100 \text{ ppb} \\ &= 132.14 \text{ ppb} \\ &= 400.27 \mu\text{g/m}^3 \end{aligned}$$

$$\begin{aligned} C_{\text{gas}} &= C_{\text{eq}} = P_o * M_i / R * T \\ &= P_o * M_i / R * T \\ &= 0.005 * 101325 * 74.08 / (8.314 * 298) \\ &= 15.148 \mu\text{g/m}^3 \end{aligned}$$

$$C_{\text{tot}} = C_{\text{eq}} + C_p$$

$$\begin{aligned} C_p &= C_{\text{tot}} - C_{\text{eq}} \\ &= 400.27 - 15.148 \\ &= 385.121 \mu\text{g/m}^3 \end{aligned}$$



## Input of SOA model

BUTENE + OH → SVBUTA (gas-phase reaction)

SVBUTA → ABUTA (aerosol module)

### Initial concentration:

SVBUTA : 132 ppb

aerosol concentration : 1e-23 ug/m<sup>3</sup>

### Parameter dataset:

Gas-phase species: SVBUTA

PM species : ABUTA

C\* : 15.14 ug/m<sup>3</sup>

Molecular weight of gas-species: 74.08 g/mol

Molecular weight of pm-species: 74.08 g/mol

### Meteorology:

T=298 K

P = 101325 pa

The model is run for one time-step

## Output from SOA model

In [32]: aa

Out [32]:

```
(array([15.14798823]),  
 array([[1.92495578e+02, 1.92495578e+02, 1.00000000e-23]]),  
 [384.9911558998439],
```

ABUTA

```
0 384.991156,  
    ABUTA
```

```
0 384.991156,  
    SVBUTA
```

```
0 15.147988,  
    SVBUTA
```

```
0 400.139144)
```

**14.8B** The biogenic hydrocarbon limonene ( $\text{C}_{10}\text{H}_{16}$ ) is a precursor to SOA. A range of products result from the OH oxidation of limonene, but for the purpose here of modeling its SOA formation it will be assumed that there are three principal products given in the table below. It is desired to model the formation of limonene SOA using the Volatility Basis Set. Limonene at a mixing ratio

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of 10 ppb (concentration =  $2.55 \times 10^{11} \text{ molecules cm}^{-3}$ ) reacts with OH. The product of the limonene-OH rate constant and the OH concentration is  $3.4 \times 10^{-4} \text{ s}^{-1}$ . The values of the saturation mass concentration at 298 K for the three assumed oxidation products are given in the table. Assume that at  $t = 0$ , an initial amount of absorbing organic aerosol  $M_o = 0.1 \mu\text{g m}^{-3}$  exists. Compute the time evolution of the concentration of each product in each volatility bin and the total organic aerosol until all the limonene is reacted and the final SOA yield.

Oxidation product	Formula	Stoichiometric coefficient	$C^*$ ( $\mu\text{g m}^{-3}$ )
Maleic acid	$\text{C}_4\text{H}_4\text{O}_4$	0.24	1
4-Isoprenyl-1-methyl-1-hydroxy-2-oxocyclohexane	$\text{C}_{10}\text{H}_{16}\text{O}_2$	0.16	0.1
Ketalimonic acid	$\text{C}_8\text{H}_5\text{O}_2$	0.04	0.01

## input in SOA model

### Gas-phase module

$LIM + OH \rightarrow 0.24 \cdot SVLIM1 + 0.16 \cdot SVLIM2 + 0.04 \cdot SVLIM3$  (gas-phase reaction)

The gas-phase module integrates following differential equations-

$$\begin{aligned} dLIM &= \int_0^t k[OH][LIM]. dt \\ dSVLIM1 &= \int_0^t 0.24 * k[OH][LIM]. dt \\ dSVLIM2 &= \int_0^t 0.16 * k[OH][LIM]. dt \\ dSVLIM3 &= \int_0^t 0.04 * k[OH][LIM]. dt \end{aligned}$$

Input of gas-phase module:

Initial concentration: [2.5e11, 0, 0, 0]

This gets updated from aerosol module.

Rate of reaction K : 3.4e-4 s-1

time-step (dt) = 0.3s

Total time = 60s

Output of gas-phase module:

Time dependent concentration of SVLIM1, SVLIM2, SVLIM3.

### Aerosol module

SVLIM1  $\rightarrow$  ALIM1

SVLIM2  $\rightarrow$  ALIM2

SVLIM3  $\rightarrow$  ALIM3

Initial concentration:

Output from gas-phase module SVLIM1, SVLIM2, SVLIM3

Initial aerosol concentration: 1e-23 ug/m3

Parameter dataset:

```
In [66]: oaspc[['name', 'gas_name', 'cstar', 'op_mw', 'og_mw']]
Out[66]:
```

	name	gas_name	cstar	op_mw	og_mw
0	ALIM1	SVLIM1	1.00	116.0	116.0
1	ALIM2	SVLIM2	0.10	168.0	168.0
2	ALIM3	SVLIM3	0.01	133.0	133.0

og\_mw is molecular weight of gas-phase species (SVLIM1, SVLIM2, SVLIM3)

op\_mw is molecular weight of aerosol-phase species (ALIM1, ALIM2, ALIM3)

Meteorology:

T=298 K

P = 101325 pa

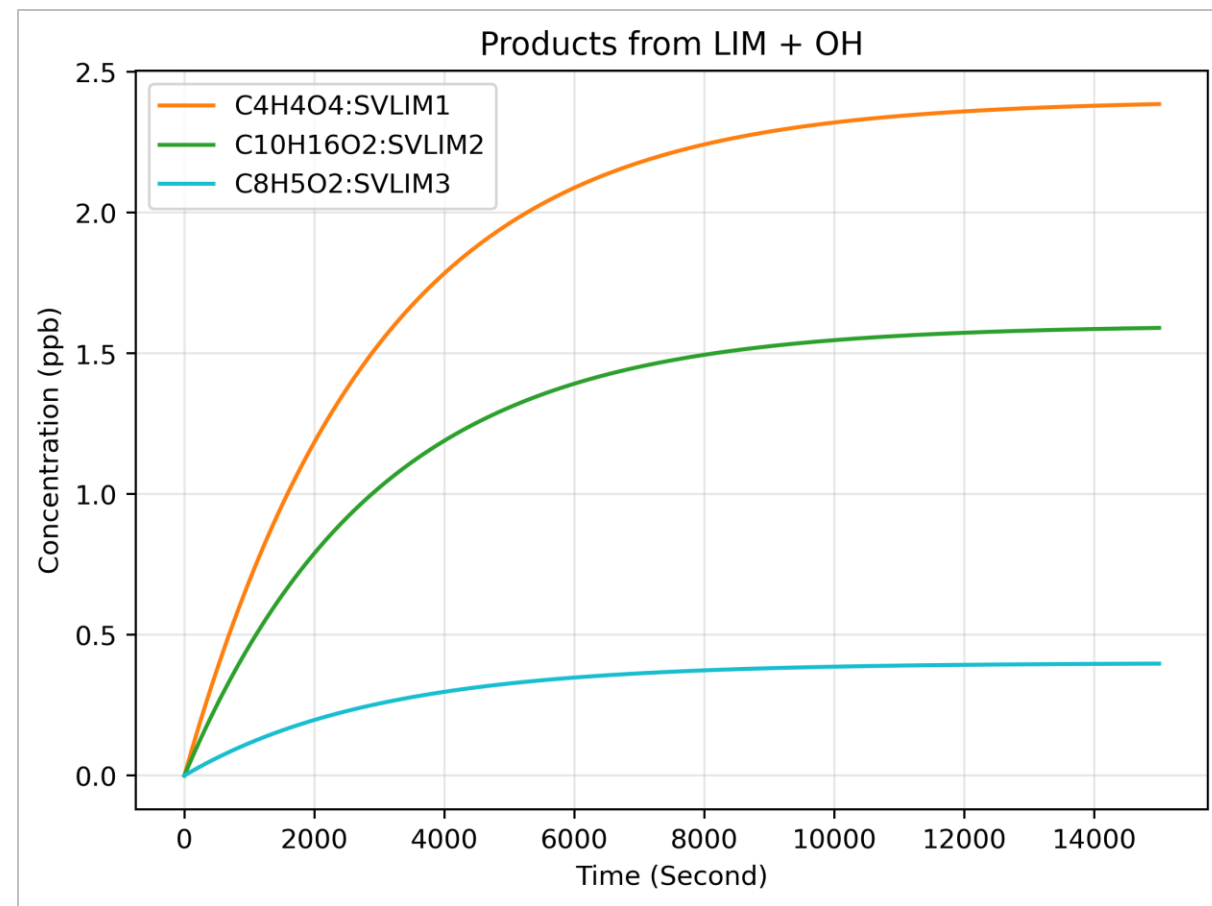
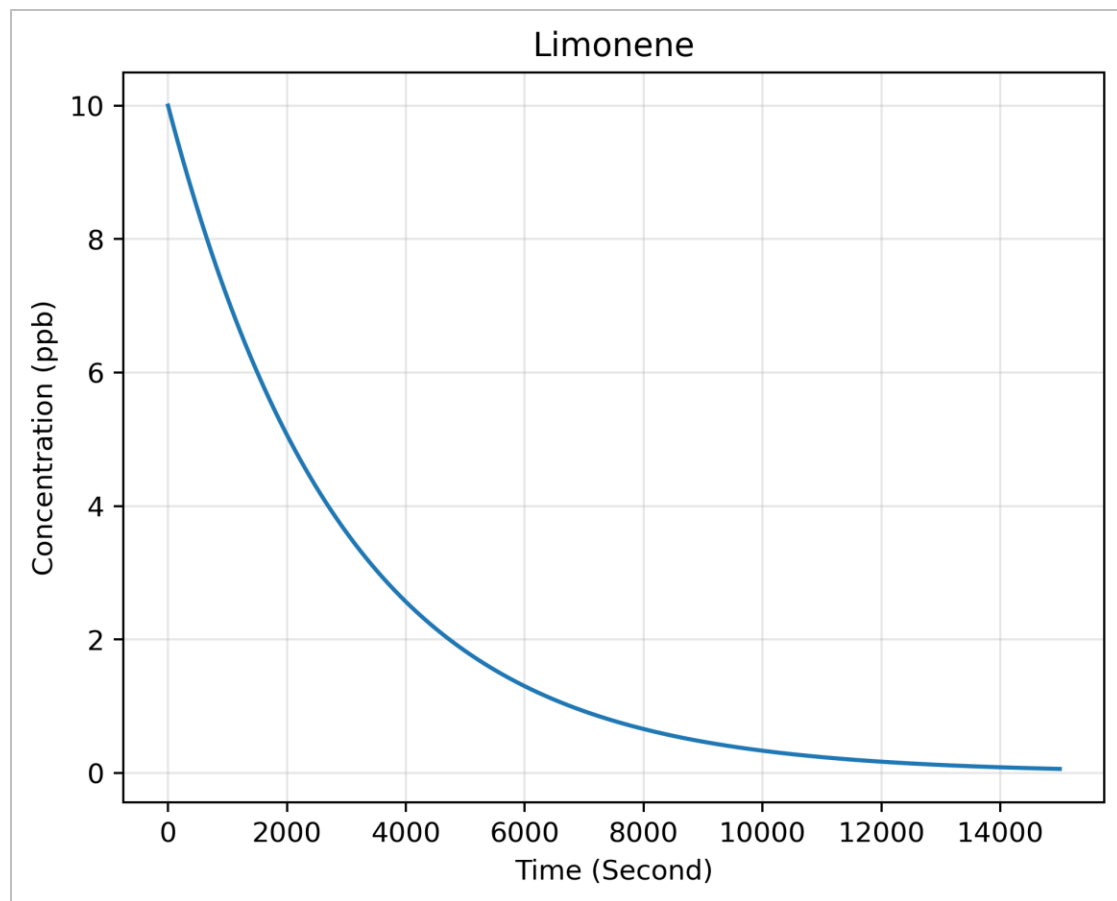
Output:

Concentration of ALIM1, ALIM2, ALIM3 in ug/m3

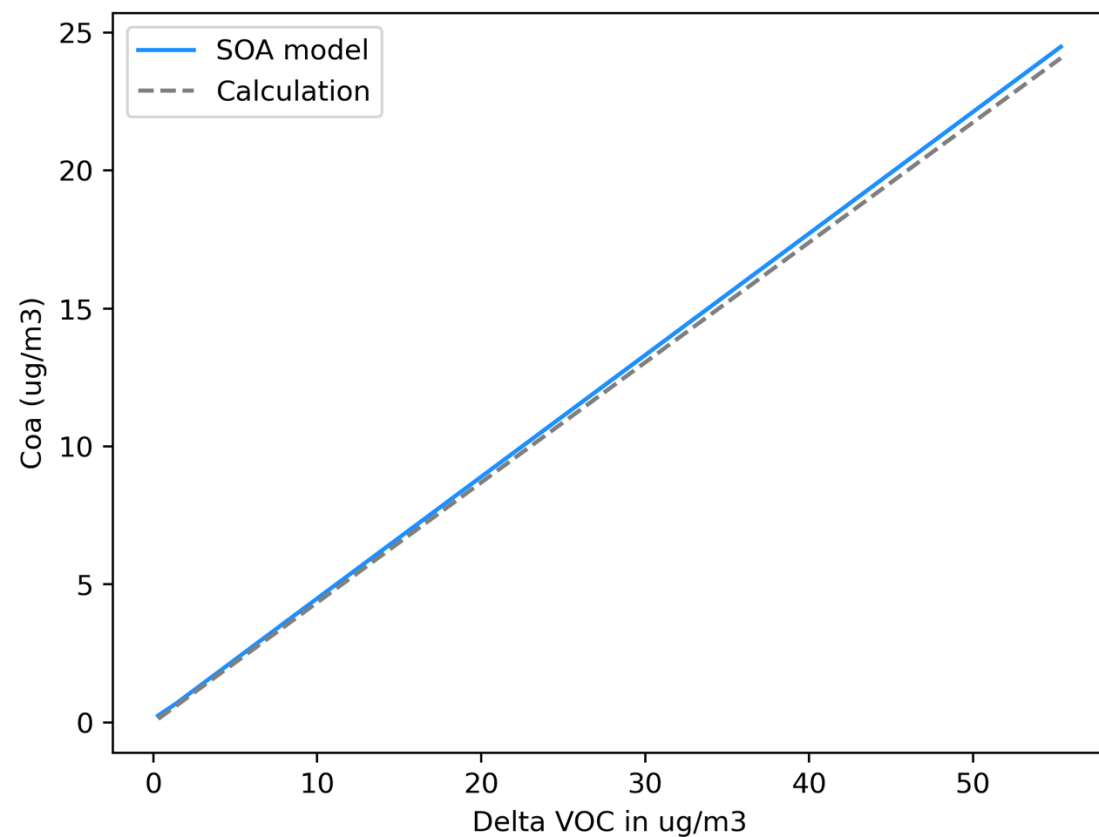
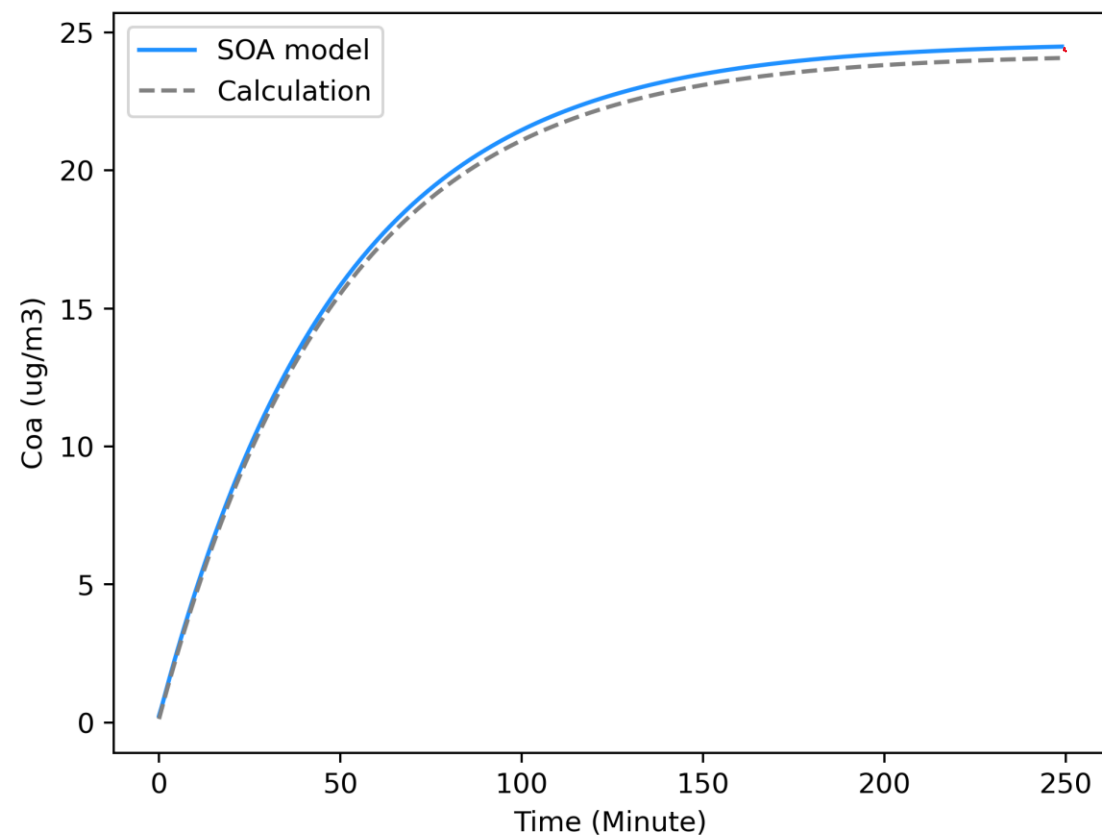
Updates SVLIM1, SVLIM2 and SVLIM3 concentration which is passed on to gas-phase module.

## Output from SOA model

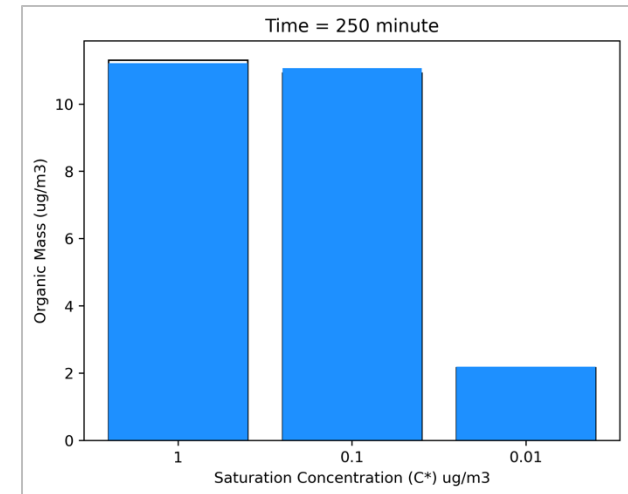
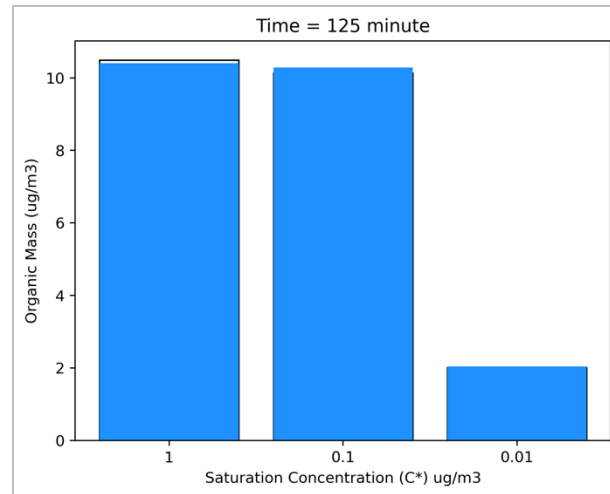
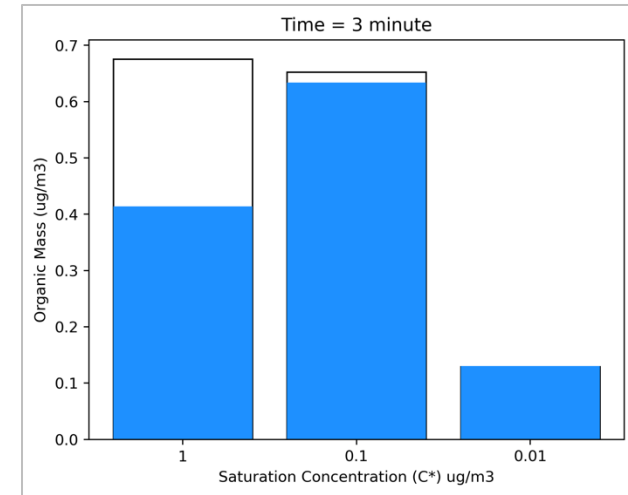
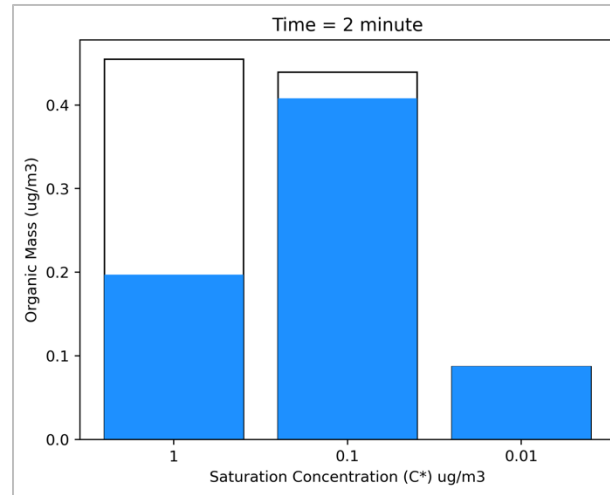
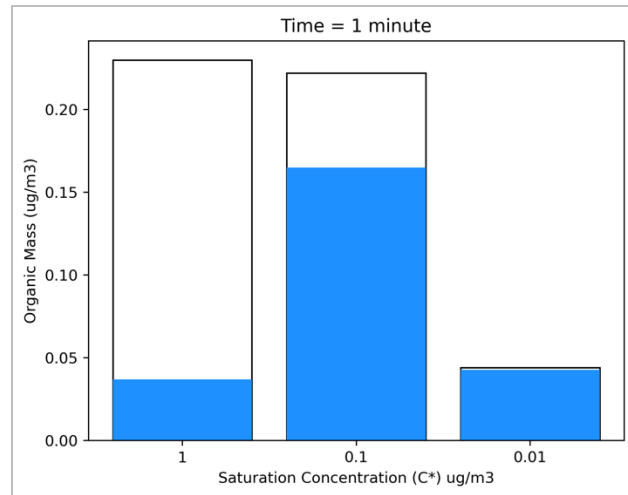
Output from the gas-phase reaction solver. These figures show as limonene decays the products are forming. This figure doesn't show the updated concentration of the gas-phase products from the aerosol module.



## Output from SOA model



## Output from SOA model



$$VOC = \alpha_1 P_1 + \alpha_2 P_2 + \dots + \alpha_n P_n$$

$$C_{tot,i} = \alpha_1 \frac{MW_i}{MW_{VOC}} \Delta VOC$$

$$C_{tot,i} = C_{aer,i} + C_{gas,i}$$

$$C_{aer,i} = C_{tot,i} - C_{gas,i}$$

$$C_{gas,i} = C_{sat,i} = C_{sat,i}^* \times X_{i,om}$$

$$C_{aer,i} = C_{tot,i} - C_{sat,i}^* \frac{C_{aer,i} / MW_i}{\sum_{j=1}^j (C_{aer,j} / MW_j) + C_{init} / MW_{init}}$$

$$C_{aer,i} = C_{tot,i} - C_{sat,i}^* \frac{C_{aer,i} / MW_i}{N}$$

$$C_{tot,i} = C_{aer,i} + C_{sat,i}^* \frac{C_{aer,i} / MW_i}{N}$$

$$C_{tot,i} = C_{aer,i} \left( 1 + \frac{C_{sat,i}^* / MW_i}{N} \right)$$

$$C_{aer,i} = C_{tot,i} \left( \frac{N \times MW_i}{N \times MW_i + C_{sat,i}^*} \right)$$

$$\frac{C_{aer,i}}{MW_i} = C_{tot,i} \left( \frac{N}{N \times MW_i + C_{sat,i}^*} \right)$$



$$N = N_{other} + \sum_{i=1}^{i=i} C_{aer,i}/MW_i$$

$$f(N) = N_{other} - N + \sum_{i=1}^{i=i} C_{aer,i}/MW_i = 0$$

$$\frac{N_{other}}{N} - 1 + \sum_{i=1}^{i=1} \frac{C_{tot,i}}{C_{sat,i}^* + MW_i \times N} = 0$$

$$upb = \sum_{i=1}^{i=i} C_{tot,i}/MW_i$$

$$lwb = \text{Nonvolatile moles}$$

$$threshold = \sum_{i=1}^{i=1} \frac{C_{tot,i}}{C_{sat,i}^*}$$

$$\frac{N_{other}}{N} - 1 + \sum_{i=1}^{i=1} \frac{C_{tot,i}}{C_{sat,i}^* + MW_i \times N} = 0$$

$$upb = \sum_{i=1}^{i=i} C_{tot,i} / MW_i$$

$lwb = \text{Nonvolatile moles}$

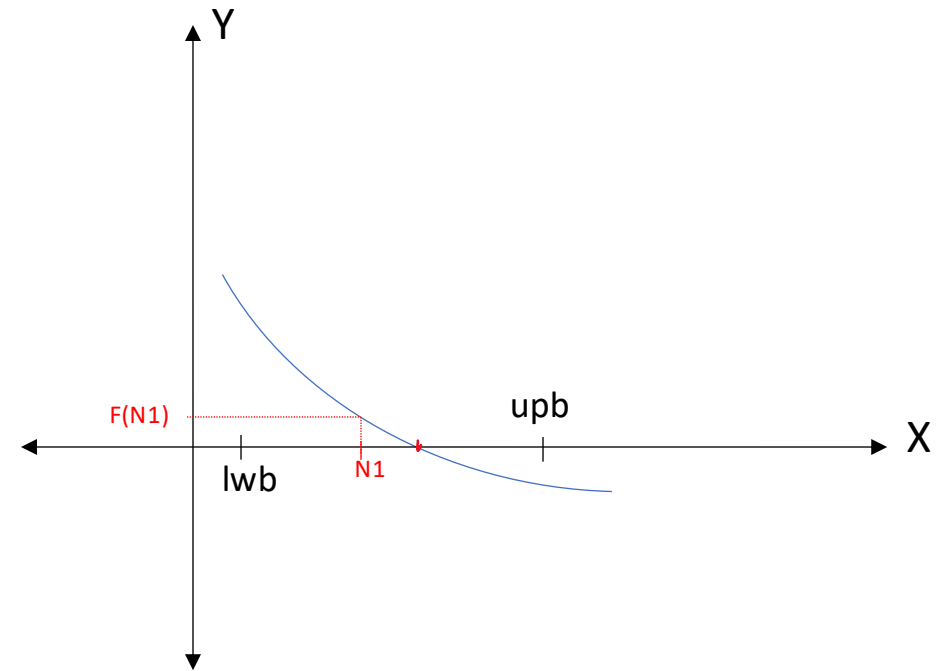
$$N1 = (lwb + upb) / 2$$

if  $f(N1)$  +ve:

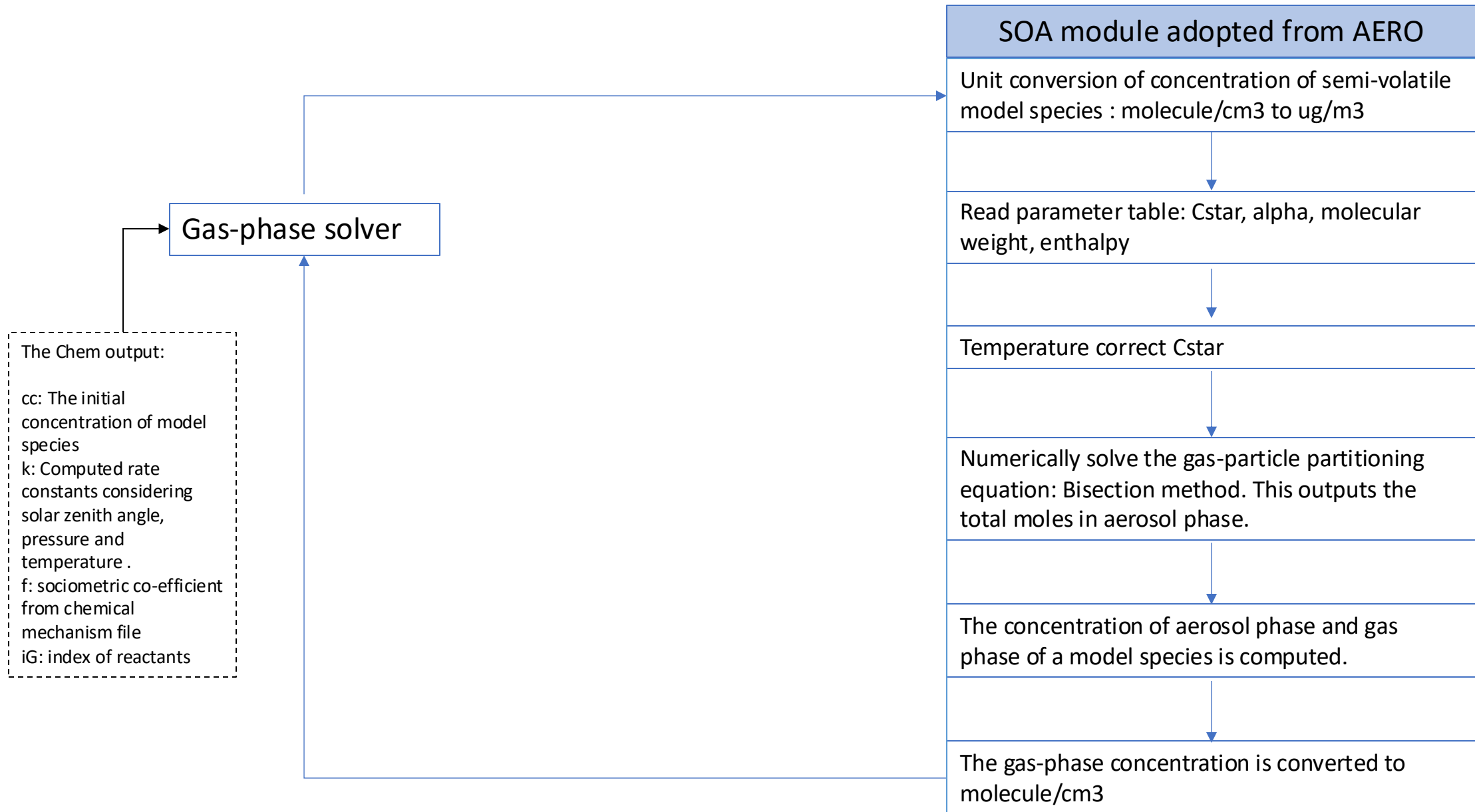
$$N2 = N1 + upb / 2$$

If  $f(N1)$  -ve:

$$N2 = N1 + lwb / 2$$



# The Gas-phase and SOA module framework



name	gas_name	ctr_name	alpha	cstar	enth	otoc	OMtoOC
{'AMT1' }	{'SVMT1' }	{'TRPRXN' }	0.04	0.01	1.02e+05	0.4	1.67
{'AMT2' }	{'SVMT2' }	{'TRPRXN' }	0.032	0.1	91000	0.4	1.67
{'AMT3' }	{'SVMT3' }	{'TRPRXN' }	0.032	1	80000	0.444	1.72
{'AMT4' }	{'SVMT4' }	{'TRPRXN' }	0.103	10	69000	0.3	1.53
{'AMT5' }	{'SVMT5' }	{'TRPRXN' }	0.143	100	58000	0.333	1.57
{'AMT6' }	{'SVMT6' }	{'TRPRXN' }	0.285	1000	47000	0.2	1.4
{'AMT7' }	{'SVMT7' }	{'TRPRXN' }	0.16	10000	36000	0.222	1.43
{'AIS01'}	{'SVIS01'}	{'ISOPRXN'}	0.232	116.01	40000	0.827	2.2
{'AIS02'}	{'SVIS02'}	{'ISOPRXN'}	0.0288	0.617	40000	0.851	2.23
{'ASQT' }	{'SVSQT' }	{'SESQRXN'}	1.537	24.984	40000	0.283	1.52
{'AAVB1'}	{'SVAVB1'}	{0x0 char }	0	0.01	18000	1.227	2.7
{'AAVB2'}	{'SVAVB2'}	{0x0 char }	0	1	18000	0.947	2.35
{'AAVB3'}	{'SVAVB3'}	{0x0 char }	0	10	18000	0.803	2.17
{'AAVB4'}	{'SVAVB4'}	{0x0 char }	0	100	18000	0.659	1.99
{'ALIM1'}	{'SVLIM1'}	{'LIMRXN' }	0.204	1	1.02e+05	0.4	1.67
{'ALIM2'}	{'SVLIM2'}	{'LIMRXN' }	0.197	0.1	1.02e+05	0.4	1.67
{'ALIM3'}	{'SVLIM3'}	{'LIMRXN' }	0.039	0.01	1.02e+05	0.4	1.67

name	gas_name	ctr_name	op_mw	og_mw	rog_mw
{ 'AMT1' }	{ 'SVMT1' }	{ 'TRPRXN' }	300	300	136
{ 'AMT2' }	{ 'SVMT2' }	{ 'TRPRXN' }	200	200	136
{ 'AMT3' }	{ 'SVMT3' }	{ 'TRPRXN' }	186	186	136
{ 'AMT4' }	{ 'SVMT4' }	{ 'TRPRXN' }	184	184	136
{ 'AMT5' }	{ 'SVMT5' }	{ 'TRPRXN' }	170	170	136
{ 'AMT6' }	{ 'SVMT6' }	{ 'TRPRXN' }	168	168	136
{ 'AMT7' }	{ 'SVMT7' }	{ 'TRPRXN' }	168	NaN	136
{ 'AIS01' }	{ 'SVIS01' }	{ 'ISOPRXN' }	132	132	68
{ 'AIS02' }	{ 'SVIS02' }	{ 'ISOPRXN' }	133	133	68
{ 'ASQT' }	{ 'SVSQT' }	{ 'SESQRXN' }	273	273	204.35
{ 'AAVB1' }	{ 'SVAVB1' }	{ 0x0 char }	198	198	NaN
{ 'AAVB2' }	{ 'SVAVB2' }	{ 0x0 char }	179	179	NaN
{ 'AAVB3' }	{ 'SVAVB3' }	{ 0x0 char }	169	169	NaN
{ 'AAVB4' }	{ 'SVAVB4' }	{ 0x0 char }	158	158	NaN
{ 'ALIM1' }	{ 'SVLIM1' }	{ 'LIMRXN' }	116	116	136.24
{ 'ALIM2' }	{ 'SVLIM2' }	{ 'LIMRXN' }	168	168	136.24
{ 'ALIM3' }	{ 'SVLIM3' }	{ 'LIMRXN' }	133	133	136.24