

### EXAMPLE\_BAT.f90

This example illustrates how to use the BAT\_SIMULATION subroutine of the Binary Activity Thermodynamic (BAT) model to predict the nonideal mixing (i.e., mole-fraction-based activity coefficients  $\gamma$ ) in binary aqueous organic systems. A binary aqueous organic system is defined as a mixture composed of one (1) organic species and its associated 'organic' water. Unlike the more sophisticated BAT calculations with phase separation consideration provided by the BAT\_INVERSION\_SIMULATION subroutine, the BAT\_SIMULATION subroutine assumes that the organic species and water are both present in the same single liquid phase.

The chemical information that the BAT\_SIMULATION subroutine needs at input is:

- 1) Elemental oxygen-to-carbon ratio of the organic species in the binary system: O: C<sub>org</sub>
- 2) Elemental hydrogen-to-carbon ratio of the organic species in the binary system (optional input): H: C<sub>org</sub>
- 3) Elemental nitrogen-to-carbon ratio of the organic species in the binary system (optional input): N: C<sub>org</sub>
- 4) Molecular weight of the organic species in the binary system (g/mol): M<sub>org</sub>
- 5) Type of oxygen-bearing functional group that represents the organic species in the binary system: Group<sub>org</sub>
- 6) Mole fraction of the organic species in the binary system: x<sub>org</sub>

Note that the mole fraction of the organic species x<sub>org</sub> in the binary mixture must be known in order to use the BAT\_SIMULATION subroutine. Since the input system is a binary mixture, the mole fraction of water x<sub>water</sub> (equal to 1.0 – x<sub>org</sub>) is also known. In other words, it is assumed that the user knows the mole fraction of the organic species that corresponds to the point where an equilibrium between the gas-phase water activity (RH) and liquid-phase water activity (a<sub>water</sub>) is reached.

The output of the BAT\_SIMULATION subroutine is the mole-fraction-based activity coefficient of the organic species ( $\gamma_{org}$ ) and of water ( $\gamma_{water}$ ) in the binary mixture.

As shown in EXAMPLE\_BAT.F90, these outputs can be used to calculate the effective concentration (i.e., the activity) of the organic species (a<sub>org</sub>) and of water (a<sub>water</sub>):

$$a_i = \gamma_i \times x_i$$

## EXAMPLE\_BAT\_INVERSION.f90

This example illustrates how to use the BAT\_INVERSION\_SIMULATION subroutine of the Binary Activity Thermodynamic (BAT) model to predict the nonideal mixing (i.e., mole-fraction-based activity coefficients  $\gamma$ ) and water uptake in a system of multiple organic species and water (i.e., an aqueous multi-organic solution). Unlike the simple BAT calculations of the BAT\_SIMULATION subroutine, the BAT\_INVERSION\_SIMULATION subroutine can determine the extent of liquid–liquid phase separation between a water-rich phase (phase  $\alpha$ ) and an organic-rich phase (phase  $\beta$ ). The BAT\_INVERSION\_SIMULATION subroutine is particularly useful in a situation where the total water mass concentration in the gas and particle phases is not known, but the relative humidity RH is. That is the typical situation encountered in 3D general circulation models and chemical transport models. As shown in EXAMPLE\_BAT.F90 file, the BAT model essentially calculates the water activity in the liquid phase for a given organic mole fraction  $x_{\text{org}}$ . In this BAT ‘inversion’ simulation, the BAT model is said to be inverted because it attempts to find the mole fraction of organic species  $x_{\text{org}}$  when only the equilibrium water activity in the liquid phase  $a_{\text{water}}$  is known (assumed to be equal to the relative humidity RH).

The information that the BAT\_INVERSION\_SIMULATION subroutine needs at input is:

- 1) Number of organic species:  $N_{\text{org}}$
- 2) Elemental oxygen-to-carbon ratio of each organic species  $j$ :  $O: C_{\text{org } j}$
- 3) Elemental hydrogen-to-carbon ratio of each organic species  $j$  (optional input):  $H: C_{\text{org } j}$
- 4) Elemental nitrogen-to-carbon ratio of each organic species  $j$  (optional input):  $N: C_{\text{org } j}$
- 5) Molecular weight of each organic species  $j$  (g/mol):  $M_{\text{org } j}$
- 6) Type of oxygen-bearing functional group that represents each organic species  $j$ :  $Group_{\text{org } j}$
- 7) Total dry mass concentration of each organic species  $j$  in the particle phase ( $\mu\text{g}/\text{m}^3$ ):  $C_{\text{org } j}^{\text{PM dry}}$
- 8) Relative humidity: RH (on a scale of 0.0 to 1.0)

The outputs of the BAT\_INVERSION\_SIMULATION subroutine are the mole-fraction-based activity coefficient of each organic species  $j$  in liquid phases  $\alpha$  ( $\gamma_{\text{org } j}^{\alpha}$ ) and  $\beta$  ( $\gamma_{\text{org } j}^{\beta}$ ), and the mass fraction of each organic species  $j$  in liquid phases  $\alpha$  ( $w_{\text{org } j}^{\alpha}$ ) and  $\beta$  ( $w_{\text{org } j}^{\beta}$ ). These mass fractions are calculated with respect to the total (all organics + water) mass concentration in liquid phases  $\alpha$  ( $C_{\text{all org + water}}^{\text{PM},\alpha}$ ) and  $\beta$  ( $C_{\text{all org + water}}^{\text{PM},\beta}$ ), respectively.

As shown in EXAMPLE\_BAT\_INVERSION.f90, these outputs can be used to calculate:

- 1) the mass concentration of each organic species  $j$  in each liquid phase ( $\mu\text{g}/\text{m}^3$ ):

$$\begin{aligned} C_{\text{org } j}^{\text{PM},\alpha} &= C_{\text{all org + water}}^{\text{PM},\alpha} \times w_{\text{org } j}^{\alpha} \\ C_{\text{org } j}^{\text{PM},\beta} &= C_{\text{all org + water}}^{\text{PM},\beta} \times w_{\text{org } j}^{\beta} \end{aligned}$$

- 2) the total organic mass concentration in each liquid phase ( $\mu\text{g}/\text{m}^3$ ):

$$C_{\text{all org}}^{\text{PM},\alpha} = \sum C_{\text{org } j}^{\text{PM},\alpha}$$

$$C_{\text{all org}}^{\text{PM},\beta} = \sum C_{\text{org } j}^{\text{PM},\beta}$$

3) the mass fraction of water in each liquid phase:

$$w_{\text{water}}^{\alpha} = 1.0 - \sum w_{\text{org } j}^{\alpha}$$

$$w_{\text{water}}^{\beta} = 1.0 - \sum w_{\text{org } j}^{\beta}$$

4) the mass fraction of water in each liquid phase ( $\mu\text{g}/\text{m}^3$ ):

$$C_{\text{water}}^{\text{PM},\alpha} = C_{\text{all org + water}}^{\text{PM},\alpha} \times w_{\text{water}}^{\alpha}$$

$$C_{\text{water}}^{\text{PM},\beta} = C_{\text{all org + water}}^{\text{PM},\beta} \times w_{\text{water}}^{\beta}$$

5) the total (organic + water) mass concentration in the particle (liquid phases  $\alpha + \beta$ ) ( $\mu\text{g}/\text{m}^3$ ):

$$C_{\text{all org + water}}^{\text{PM},\alpha+\beta} = C_{\text{all org + water}}^{\text{PM},\alpha} + C_{\text{all org + water}}^{\text{PM},\beta}$$

6) the fractional liquid–liquid partitioning of each organic species j to each liquid phase:

$$q_{\text{org } j}^{\alpha} = \frac{C_{\text{org } j}^{\text{PM},\alpha}}{C_{\text{all org}}^{\text{PM},\alpha} + C_{\text{all org}}^{\text{PM},\beta}}$$

$$q_{\text{org } j}^{\beta} = \frac{C_{\text{org } j}^{\text{PM},\beta}}{C_{\text{all org}}^{\text{PM},\alpha} + C_{\text{all org}}^{\text{PM},\beta}}$$

7) the instantaneous effective saturation concentration of each organic species j to each liquid phase ( $\mu\text{g}/\text{m}^3$ ) (when the pure component saturation mass concentration of each organic species j at the temperature of interest is known):

$$C_{\text{org } j}^{*,\alpha} = \frac{C_{\text{org } j}^{\text{sat}} \times C_{\text{all org + water}}^{\text{PM},\alpha+\beta} \times \gamma_{\text{org } j}^{\alpha} \times q_{\text{org } j}^{\alpha}}{M_{\text{org } j} \times \left[ \left( \sum \frac{C_{\text{org } j}^{\text{PM},\alpha}}{M_{\text{org } j}} \right) + \frac{C_{\text{water}}^{\text{PM},\alpha}}{M_{\text{water}}} \right]}$$

$$C_{org\ j}^{*,\beta} = \frac{C_{org\ j}^{sat} \times C_{all\ org + water}^{PM,\alpha+\beta} \times \gamma_{org\ j}^{\beta} \times q_{org\ j}^{\beta}}{M_{org\ j} \times \left[ \left( \sum \frac{C_{org\ j}^{PM,\beta}}{M_{org\ j}} \right) + \frac{C_{water}^{PM,\beta}}{M_{water}} \right]}$$

8) the mean instantaneous effective saturation concentration of each organic species j ( $\mu\text{g}/\text{m}^3$ ):

$$C_{org\ j}^* = C_{org\ j}^{*,\alpha} \times q_{org\ j}^{\alpha} + C_{org\ j}^{*,\beta} \times q_{org\ j}^{\beta}$$

9) the hygroscopicity parameter kappa of the organic aerosol  $\kappa_{org}^{HGF}$  only from BAT water uptake calculations (before VBS):

a) the cumulative contribution of organic component volumes at a given relative humidity RH:

$$V_{org} = \frac{\sum (C_{org\ j}^{PM,\alpha} + C_{all\ org}^{PM,\beta})}{\rho_{org\ j}}$$

b) the cumulative contribution of water volume at a relative humidity RH > 0.0:

$$V_{water} = \frac{\sum (C_{water}^{PM,\alpha} + C_{water}^{PM,\beta})}{\rho_{water}}$$

c) the liquid-phase water activity is equal to the gas-phase water activity (RH) for bulk equilibrium simulation:

$$a_{water} = RH$$

d) the hygroscopicity parameter kappa of the organic aerosol  $\kappa_{org}^{HGF}$ :

$$\kappa_{org}^{HGF} = \left( \frac{1.0}{a_{water}} - 1.0 \right) \times \left( \frac{V_{water}}{V_{org}} \right)$$

### EXAMPLE\_BAT\_INVERSION\_VBS.f90

This example illustrates how to use the BAT\_INVERSION\_VBS\_SIMULATION subroutine of the Binary Activity Thermodynamic (BAT) model to predict the equilibrium mass concentration of each organic species and of water in an aqueous multi-organic solution. Just like the BAT calculations of the BAT\_INVERSION\_SIMULATION subroutine, the BAT\_INVERSION\_VBS\_SIMULATION subroutine can determine the extent of liquid–liquid phase separation between a water-rich phase (phase  $\alpha$ ) and an organic-rich phase (phase  $\beta$ ). The BAT\_SIMULATION\_VBS\_INVERSION subroutine is also particularly useful in a situation where the total water mass concentration in the gas and particle phases is not known, but the relative humidity RH is. That is the typical situation encountered in 3D general circulation models and chemical transport models. The BAT model is said to be inverted because it attempts to find the mole fraction of organic species  $x_{\text{org}}$  when only the equilibrium water activity in the liquid phase  $a_{\text{water}}$  is known (assumed to be equal to the relative humidity RH). In this case, the BAT (inversion) calculations are coupled with a VBS partitioning scheme that considers nonideality and liquid–liquid equilibria, as outlined in Section 2 of Gorkowski et al., 2019.

The information that the BAT\_INVERSION\_SIMULATION subroutine needs at input is:

- 1) Number of organic species:  $N_{\text{org}}$
- 2) Elemental oxygen-to-carbon ratio of each organic species  $j$ :  $O: C_{\text{org } j}$
- 3) Elemental hydrogen-to-carbon ratio of each organic species  $j$  (optional input):  $H: C_{\text{org } j}$
- 4) Elemental nitrogen-to-carbon ratio of each organic species  $j$  (optional input):  $N: C_{\text{org } j}$
- 5) Molecular weight of each organic species  $j$  (g/mol):  $M_{\text{org } j}$
- 6) Type of oxygen-bearing functional group that represents each organic species  $j$ :  $Group_{\text{org } j}$
- 7) Pure component saturation mass concentration of each organic species  $j$  at the temperature of interest ( $\mu\text{g}/\text{m}^3$ ):  $C_{\text{org } j}^{\text{sat}}$
- 8) Mass concentration of each organic species  $j$  in the gas phase + particle phase ( $\mu\text{g}/\text{m}^3$ ):  $C_{\text{org } j}^{\text{gas+particle}}$
- 9) Relative humidity: RH (on a scale of 0.0 to 1.0)

The output of the BAT\_INVERSION\_VBS\_SIMULATION subroutine is the equilibrium mass concentration of water and of each organic species  $j$  in liquid phases  $\alpha$  ( $C_{\text{water}}^{\text{PM},\alpha}, C_{\text{org } j}^{\text{PM},\alpha}$ ) and  $\beta$  ( $C_{\text{water}}^{\text{PM},\beta}, C_{\text{org } j}^{\text{PM},\beta}$ ).

As shown in EXAMPLE\_BAT\_INVERSION\_VBS.F90, these outputs can be used to calculate:

- 1) the total (organic + water) equilibrium mass concentration in liquid phases  $\alpha$  and  $\beta$  ( $\mu\text{g}/\text{m}^3$ ):

$$C_{\text{all org+water}}^{\text{PM},\alpha} = \sum C_{\text{org } j}^{\text{PM},\alpha} + C_{\text{water}}^{\text{PM},\alpha}$$

$$C_{\text{all org+water}}^{\text{PM},\beta} = \sum C_{\text{org } j}^{\text{PM},\beta} + C_{\text{water}}^{\text{PM},\beta}$$

- 2) the total (organic + water) equilibrium mass concentration in the particle (liquid phase  $\alpha + \beta$ ) ( $\mu\text{g}/\text{m}^3$ ):

$$C_{\text{all org} + \text{water}}^{\text{PM}, \alpha + \beta} = C_{\text{all org} + \text{water}}^{\text{PM}, \alpha} + C_{\text{all org} + \text{water}}^{\text{PM}, \beta}$$

- 3) the hygroscopicity parameter kappa of the organic aerosol  $\kappa_{\text{org}}^{\text{HGF}}$ , related to the hygroscopic growth factor of the organic mixture as a function of composition (and indirectly RH) (after VBS):
- a) the cumulative contribution of organic component volumes at a given relative humidity RH:

$$V_{\text{org}} = \frac{\sum (C_{\text{org } j}^{\text{PM}, \alpha} + C_{\text{all org}}^{\text{PM}, \beta})}{\rho_{\text{org } j}}$$

- b) the cumulative contribution of water volume at relative humidity  $\text{RH} > 0.0$ :

$$V_{\text{water}} = \frac{\sum (C_{\text{water}}^{\text{PM}, \alpha} + C_{\text{water}}^{\text{PM}, \beta})}{\rho_{\text{water}}}$$

- c) the liquid-phase water activity is equal to the gas-phase water activity (RH) for bulk equilibrium simulation:

$$a_{\text{water}} = \text{RH}$$

- d) the hygroscopicity parameter kappa of the organic aerosol  $\kappa_{\text{org}}^{\text{HGF}}$ :

$$\kappa_{\text{org}}^{\text{HGF}} = \left( \frac{1.0}{a_{\text{water}}} - 1.0 \right) \times \left( \frac{V_{\text{water}}}{V_{\text{org}}} \right)$$