Effect of Turbulence on Atmospheric Chemistry for non-constant reaction rate.

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The transport equation for N reacting species q_i

$$\frac{\partial q_i}{\partial t} + u_\alpha \frac{\partial q_i}{\partial x_\alpha} = \alpha_{ij} q_i q_j \qquad (1)$$

contains a right-hand-side non-linear term responsible for chemical transformations. α_{ij} are elements of a symmetric matrix of rates of chemical reaction between species ***i*** and ***j***. Summation is conducted on all repeating indexes. Index $\boldsymbol{\alpha}$ equal to 1, 2, 3 and indexes ***i*** and ***j*** change from 1 to N. In /Shnaydman, Stenchikov,2005/ we assume that chemical rate transformations α_{ij} are constant.

Now we developed the closure scheme of mean concentration calculation for the case when rate reaction depends on temperature. For the simplicity we suppose that the reaction rate is a linear function of the temperature

$$\alpha_{ij} = \alpha_0 (T/T_0). \qquad (2)$$

The application of the Reynolds averaging leads to the following transport-diffusion equation

$$\frac{\partial \bar{q}_i}{\partial t} + \bar{u}_\alpha \frac{\partial \bar{q}_i}{\partial x_\alpha} = \underbrace{\frac{\partial}{\partial x_\beta} K_L \frac{\partial \bar{q}_i}{\partial x_\beta}}_{(1)} + \underbrace{\frac{\partial}{\partial x_3} K_Z \frac{\partial \bar{q}_i}{\partial x_3}}_{(2)} +$$

$$\frac{\partial}{\partial x_\alpha} \gamma \frac{\partial \bar{q}_i}{\partial x_\alpha} - \underbrace{\alpha_0 (\bar{T}/T_0)(\bar{q}_i \bar{q}_j) + \alpha_0 (\bar{T}/T_0)(\overline{q'_i q'_j})}_{(3)} -$$

$$\underbrace{\frac{\alpha_0}{T_0}(\overline{T' q'_i}\,\bar{q}_j, + \overline{T' q'_j}\,\bar{q}_i + \overline{T' q'_i q'_j})}_{(4)} \qquad (3)$$

The effect of turbulence on the temporal evolution of mean concentration is given by the vertical (1) and horizontal (2) diffusion , chemical interaction between reacting species(3) and temperature influence on the reaction rate in the turbulent enronviment.

The input heat equation for potential temperature and transport-diffusion mean concentration equations are used for definition of mixed temperature-concentration covariance. and the temperature variance

$$\frac{\partial \overline{T' q'_i}}{\partial t} + \bar{u}_\alpha \frac{\partial \overline{T' q'_i}}{\partial x_\alpha} = \frac{\partial}{\partial x_\beta} K_L \frac{\partial \overline{T' q'_i}}{\partial x_\beta} + \frac{\partial}{\partial x_3} K_Z \frac{\partial \overline{T' q'_i}}{\partial x_3} +$$

$$2(K_L \frac{\partial \bar{q}_i}{\partial x_\beta}\frac{\partial \bar{T}}{\partial x_\beta} + K_Z \frac{\partial \bar{q}_i}{\partial x_3}\frac{\partial \bar{\theta}}{\partial x_3}) - \alpha_0 (\bar{q}_i \overline{T' q'_j} + \bar{q}_j \overline{T' q'_i}) + \frac{\alpha_0}{T_0}(\overline{T'^2}\,\bar{q}_i \bar{q}_j) -$$

(1)

$$\alpha_0 (\overline{T' q'_i q'_j}) - \frac{\alpha_0}{T_0}(\overline{T'^2 q'_i}\,\bar{q}_j + \overline{T'^2 q'_j}\,\bar{q}_i) - \frac{\alpha_0}{T_0}(\overline{T'^2 q'_i q'_j}), \qquad (4)$$

(2)

In (4) the additional terms related with temperature variance (1)., third and fourth mixed moments (2) are appeared. The first additional term is defined by using the equation of temperature variance.

$$\frac{\partial \overline{T'^2}}{\partial t} + \bar{u}_\alpha \frac{\partial \overline{T'^2}}{\partial x_\alpha} = \frac{\partial}{\partial x_\beta} K_L \frac{\partial \overline{T'^2}}{\partial x_\beta} + \frac{\partial}{\partial x_3} K_Z \frac{\partial \overline{T'^2}}{\partial x_3} + 2(K_L \frac{\partial \bar{T}}{\partial x_\beta}\frac{\partial \bar{T}}{\partial x_\beta} + K_Z \frac{\partial \bar{\theta}}{\partial x_3}\frac{\partial \bar{\theta}}{\partial x_3}) \quad (5)$$

Follow /Petersen et. al./, we wrote the closure parameterization for the third and fourth moments.

$$\overline{q'_i q'^2_j} = \mathbf{C}\,\tau\,(\overline{u'_\alpha q'_i}\frac{\partial \overline{q'^2_j}}{\partial x_\alpha} + \overline{u'_\alpha q'^2_j}\frac{\partial \bar{q}_i}{\partial x_\alpha})$$

$$\overline{T' q'_i q'_j} = -\mathbf{C}\,\tau\,(\overline{u'_\beta T'}\frac{\partial \overline{q'_i q'_j}}{\partial x_\beta} + \overline{u'_3 \vartheta'}\frac{\partial \overline{q'_i q'_j}}{\partial x_3} + \overline{u'_\alpha q'_i q'_j}\frac{\partial \bar{T}}{\partial x_\alpha}) \qquad (6)$$

$$\overline{T'^2 q'_i} = -\mathbf{C}\,\tau\,(\overline{u'_\beta T'}\frac{\partial \overline{T' q'_i}}{\partial x_\beta} + \overline{u'_3 \theta'}\frac{\partial \overline{T' q'_i}}{\partial x_3} + \overline{u'_\alpha T' q'_i}\frac{\partial \bar{T}}{\partial x_\alpha}) \quad \tau = E/\varepsilon$$

$$\overline{T'^2 q'_i q'_j} = -\mathbf{C}\,\tau\,(\overline{u'_\alpha T'^2}\frac{\partial \overline{q'_i q'_j}}{\partial x_\alpha} + + \overline{u'_\alpha q'_i q'_j}\frac{\partial \overline{T'^2}}{\partial x_\alpha})$$

$\tau = E/\varepsilon$, $-\overline{u_i S'} = K_m \frac{\partial \bar{S}}{\partial x_i}$ S= q_i, q_j, T , their variances,second, third and fourth moments, $K_m = K_L$, if i=1,2 and $K_m = K_Z$, T=θ if i=3

where E is the turbulent kinetic energy and epsilon is the dissipation rate. These values are obtained from two-equation closure scheme/Shnaydman, 2004 / based on the turbulent kinetic energy and dissipation rate prediction equations.

The developed model of the transport and turbulent diffusion of reacting species together with improved two-equation turbulence closure scheme including the main mechanisms of spreading the pollutants will be applied for estimation of atmospheric pollution characteristics.

Petersen, A.C.,Beets, C.H., H.van Dop, Duynkerke, P.G., Siebesma,A.P., Mass-flux characteristics of reactive scalars in the convective boundary layer. J. Atmos. Sci.,56,37-56,1999.

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