

# On the Algorithm of Calculation of the Equilibrium Gas-phase Concentration at the Particle Surface in the Kinetic Models of Aerosol Dynamics

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**Abstract.** The paper is dedicated to the description of the algorithm of calculation of the equilibrium gas-phase concentration at the surface of the aerosol particle – a parameter, which defines the rate of mass transport between the gas and aerosol phases in the kinetic models of atmospheric aerosol dynamics. Some problems concerning deducing of the surface equilibrium gas-phase concentrations from thermodynamic equilibrium aerosol models are discussed. It is shown that computational algorithm should be split in two steps; the sought quantity is defined on the second step, after ion concentration calculation.

## 1 Introduction

Aerosol dynamics simulation is a consistent part of air quality models, which provide a prediction of the spatial and temporal distributions of pollutant species resulting from emissions, advection, diffusion, dry deposition and chemical reaction. Traditionally the mass, composition, and size distribution of the volatile inorganics in atmospheric aerosol have been predicted assuming local thermodynamic equilibrium between the aerosol and gas phases. Nevertheless investigations show that under typical atmospheric conditions the volatile inorganics are not in equilibrium with the aerosol and both mass transfer and thermodynamic considerations determine their size distribution [1]. In [2] 3 different models to the treatment of mass transfer between the bulk gas phase and the surface of atmospheric particles were compared. It was shown that only in kinetic model, where mass transfer is simulated explicitly, chemical concentrations in the bulk gas phase and in the particles may or may not be in equilibrium. The rate of mass transport between the gas and aerosol phases in kinetic model is dependent upon the value of equilibrium gas-phase concentration at the surface of the aerosol particle, which in turn depends upon the particle size. Equilibrium gas-phase concentration can be deduced either with the help of Henry 's law constant for gas/liquid equilibrium, or using thermodynamic equilibrium aerosol models [2]. However using both approaches in kinetic aerosol models is connected with some difficulties. In case of dissociation reactions (the most frequent in the

atmosphere) we should use effective or pseudo Henry's constants [3] that depend upon the hydrogen ion concentration, the value, which is a priori unknown, and have to be calculated from different considerations. The use of the equilibrium thermodynamic models in case of kinetic models also needs some special approach, connected with reformulation of system of chemical equations and input/output parameters. The paper is dedicated to the description of such an approach, connected with splitting the calculation of the chemical reactions in aqueous phase and equilibrium gas/aqueous phase reactions in two steps.

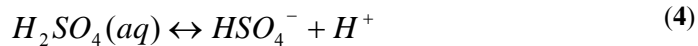
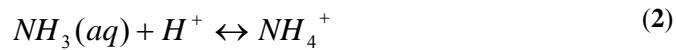
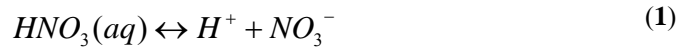
## 2 Model Description

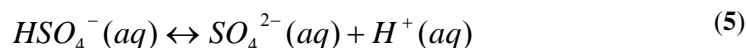
Calculations of the interfacial mass transport is based upon the proportionality of the mass flow of species  $i$  to the term  $(p_{i,\infty} - p_{i,s})$ , where  $p_{i,\infty}$ ,  $p_{i,s}$  are the atmospheric partial pressure and the particle surface vapor pressure respectively. We assume that if aerosol particle consists of more than one phase, these phases are in thermodynamic equilibrium. It is considered that solid phases do not form until very low relative humidities are reached and therefore aerosol is completely aqueous.

Thermodynamic equilibrium chemical model PEQIONH (Pressure EQUilibrium and ION concentration calculation using Henry's law constants) was developed for prediction of equilibrium pressures of chemical components in case of kinetic approach, where chemical concentrations in the bulk gas phase and in the particles may or may not be in equilibrium.

Unlike the other thermodynamic models, intended for calculation concentrations of each phase being in equilibrium with each other, and using total amount of chemical species in gas, liquid and solid phases as an input parameter, in case of kinetic approach we do not know a priori total concentration, but have to use aqueous concentrations of undissociated chemical species as a model input. This requires reformulation of the system of model equations. We have to withdraw mass balance equations and to add equations describing dissociation reactions in the liquid phase.

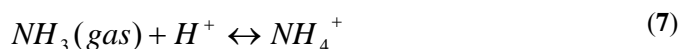
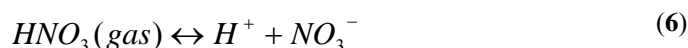
In the PEQIONH model algorithm of chemical equation calculation is split in two steps. At the first step the following set of equilibrium dissociation reactions in aqueous phase are considered:





where designation (*aq*) refers to unassociated values of aqueous chemical species. Taken values of  $H_2SO_4(aq)$ ,  $HNO_3(aq)$ ,  $NH_3(aq)$  as an input, ionic concentrations in aqueous phase are calculated.

At the second step the following equilibrium gas/aqueous phase reactions are considered.



Using ionic concentrations obtained at the first calculation step and corresponding reaction constants (the Henry's law constants) the system of equations allows to obtain equilibrium values of ammonium and nitric acid vapor pressures ( $NH_3(gas)$  and  $HNO_3(gas)$ ) consequently.

Numerical solution of the system of equations (1)–(7) is based upon the 4 steps iterative algorithm proposed by Jacobson [4] with the only exception that all concentrations of gas, aqueous and ionic species were set in mol/(m<sup>3</sup> air).

### 3 Model Sensitivity Studies

The model was used to simulate equilibrium concentrations of sulfate, nitrate, ammonia, aerosol liquid water content and saturation pressure values of ammonia and nitric acid under various input concentrations, which vary from a low value of 5 µg/m<sup>3</sup> up to 45–70 µg/m<sup>3</sup>. Input conditions together with simulation results obtained by PEQION and for comparison by three other chemical equilibrium models KEQUIL [7], EQUIL [8] and MARS [6] are presented in Table 1.

**Table 1.** Aerosol-phase concentrations in µg/m<sup>3</sup> predicted by various equilibrium models at 298 K, RH = 0,9

N	TS	TN	TA	Ammonium				Nitrate			
				1	1	2	3	4	2	3	4
1	40	45	70	24,0	36,7	44,2	44,2	44,2	27,6	27,6	27,6
2	40	45	12	12,4	13,8	7,0	7,5	6,8	12,7	12,7	12,7
3	40	45	10	10,4	9,5	3,8	4,3	4,2	10,6	10,6	10,6
4	40	45	5	5,3	2,9	0,7	0,8	0,8	5,3	5,3	5,3
5	40	5	12	12,0	1,1	1,4	1,5	1,5	12,6	12,6	12,7
6	40	5	10	10,3	0,6	0,6	0,7	0,7	10,5	10,5	10,6
7	5	45	5	4,9	14,2	11,7	11,9	11,2	5,1	5,1	5,1
8	5	5	5	1,8	0,71	3,1	3,3	3,2	2,7	2,8	2,8

where 1,2,3,4 – model types: PEQIONH, KEQUIL, EQUIL and MARS consequently, RH – relative humidity value, TS, TN, TA – are total input sulfate, nitrate and ammonia concentrations in  $\mu\text{g}/\text{m}^3$  consequently.

As it is evident from Table 1 PEQIONH model demonstrates very good agreement with the other equilibrium model results regarding ammonia and sulfur concentration and more or less satisfactory results in case of nitric concentrations. The largest differences between PEQIONH and other models appear while nitrate concentration simulation in case of small amount of the input ammonia and when the input total nitrate was relatively large or equal to the rest input parameters. That can be caused both by insufficient number of chemical equations used in PEQIONH model describing the interaction of the nitrates with the other chemical species and neglect of the solid phase presence.

The main purpose for model PEQIONH development was its incorporation into aerosol microphysical block for proper simulation of chemical composition of aerosol particles and gas/particle mass transfer processes in case of kinetic approach to the treatment of mass transfer between the bulk gas phase and the surface of atmospheric particles. PEQIONH model was used to calculate saturation vapor pressure of the chemical components at the surface of the particles and to calculate ion concentrations resulted from dissociation process.

To test coupled model (PEQIONH + microphysics) applicability it should be compared with the model, using the same kinetic approach Zhang [2]. The difficulty was that Zhang results were not provided with the data concerning temperature and relative humidity at which they were achieved. We had to vary corresponding parameters to find conditions where result coincidence might have take place. Corresponding results are given in table 2.

Table 2. Total ion and summary (ion + undissociated species ) mass concentrations of chemical species in the aqueous phase. Comparison results obtained in PEQIONH + MICROPHYSICS and ZHANG models.

CS	Zhang	PEQIONH + MICROPHYSICS								
		T = 288K			T = 298K			T = 300K		
		RH	RH	RH	RH	RH	RH	RH	RH	RH
		90%	80%	50%	90%	80%	50%	90%	80%	50%
NO <sub>3</sub> <sup>-</sup> HNO <sub>3</sub>	17,7	18,2 19,7	16,0 18,6	10,8 16,0	13,7 17,4	9,4 15,2	3,4 12,2	12,4 16,8	8,1 14,6	2,6 11,7
NH <sub>4</sub> <sup>+</sup> NH <sub>3</sub>	11,2	12,1 20,1	11,2 19,8	9,2 19,1	10,5 19,5	9,0 18,9	6,7 18,1	10,1 19,3	8,6 18,7	6,4 18,0
SO <sub>4</sub> <sup>2-</sup> + HSO <sub>4</sub> <sup>-</sup> H <sub>2</sub> SO <sub>4</sub>	20,0	19,6 20,0	19,6 20,0	19,6 20,0	19,6 20,0	19,6 20,0	19,6 20,0	19,6 20,0	19,6 20,0	19,6 20,0

CS – chemical species concentrations in  $\mu\text{g}/\text{m}^3$ , T – temperature, RH – relative humidity, summary concentration values are in the second line of each cell.

As it is evident from Table 2, there is rather good agreement in ion concentrations of the condensable species obtained with the help of the two models in the following range of atmospheric conditions: temperature between 288K and 298K at RH = 90%, and RH between 80% and 90% at T = 288K.

Calculations, conducted with the help of PEQIONH + MICROPHYSICS model show that at all conditions ion concentrations are less than summary (ion + undissociated ) concentrations. So it should be concluded that HNO<sub>3</sub>, NH<sub>3</sub> did not dissociate completely in aerosol particles, opposite to H<sub>2</sub>SO<sub>4</sub> that presented practically fully in dissociated state.

## 4 Conclusions

Thermodynamic equilibrium chemical model PEQIONH was developed for prediction of equilibrium pressures of chemical components in case of kinetic approach to aerosol dynamics simulation, where chemical concentrations in the bulk gas phase and in the particles may or may not be in equilibrium. System of equilibrium chemical equations was reformulated to have aqueous concentrations of undissociated chemical species as a model input. Calculation of the chemical reactions in aqueous phase and equilibrium gas/aqueous phase reactions were split in two steps, the sought value of the equilibrium gas-phase concentration at the surface of the aerosol particle was defined on the second step, after ion concentration calculation. Comparison test studies showed good agreement of the results obtained by PEQIONH model with the results obtained by the other equilibrium models and with the models, using the same kinetic approach.

## 5 Acknowledgments

This work was fulfilled in the frame of the ISTC Project N 2834.

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