Atmospheric Environment 133 (2016) 34–40

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Analytical expression for gas-particle equilibration time scale and its numerical evaluation

Tatu Anttila [a, b, *], Kari E.J. Lehtinen [c, d], Miikka Dal Maso [a]

[a] Tampere University of Technology, Department of Physics, P.O. Box 527, FI-33101 Tampere, Finland
[b] Finnish Meteorological Institute, Research and Development, P.O. Box 503, FI-00101 Helsinki, Finland
[c] Finnish Meteorological Institute, Atmospheric Research Centre of Eastern Finland, P.O. Box 1627, FI-70211 Kuopio, Finland
[d] Department of Applied Physics, University of Eastern Finland, P.O. Box 1627, FI-70211 Kuopio, Finland

HIGHLIGHTS

- A simple formula for estimating gas/particle partitioning time scale was derived.
- The derived equation was tested extensively against numerical simulations.
- Under certain conditions, some previous estimates for the time scale for gas/particle equilibration time scale may give erroneous estimates.

ARTICLE INFO

Article history:
Received 24 September 2015
Received in revised form
1 March 2016
Accepted 9 March 2016
Available online 12 March 2016

Keywords:
Secondary organic aerosol
Gas/particle partitioning
Semi-volatile compounds
Time scale analysis

ABSTRACT

We have derived a time scale τ_{eq} that describes the characteristic time for a single compound i with a saturation vapour concentration $C_{eff,i}$ to reach thermodynamic equilibrium between the gas and particle phases. The equilibration process was assumed to take place via gas-phase diffusion and absorption into a liquid-like phase present in the particles. It was further shown that τ_{eq} combines two previously derived and often applied time scales τ_a and τ_s that account for the changes in the gas and particle phase concentrations of i resulting from the equilibration, respectively. The validity of τ_{eq} was tested by comparing its predictions against results from a numerical model that explicitly simulates the transfer of i between the gas and particle phases. By conducting a large number of simulations where the values of the key input parameters were varied randomly, it was found out that τ_{eq} yields highly accurate results when i is a semi-volatile compound in the sense that the ratio of total (gas and particle phases) concentration of i to the saturation vapour concentration of i, μ, is below unity. On the other hand, the comparison of analytical and numerical time scales revealed that using τ_a or τ_s alone to calculate the equilibration time scale may lead to considerable errors. It was further shown that τ_{eq} tends to overpredict the equilibration time when i behaves as a non-volatile compound in a sense that $\mu > 1$. Despite its simplicity, the time scale derived here has useful applications. First, it can be used to assess if semi-volatile compounds reach thermodynamic equilibrium during dynamic experiments that involve changes in the compound volatility. Second, the time scale can be used in modeling of secondary organic aerosol (SOA) to check whether SOA forming compounds equilibrate over a certain time interval.

1. Introduction

A significant fraction of aerosol residing in the troposphere consists of organic matter (Kanakidou et al., 2005). There are two types of aerosol sources: primary, i.e. aerosol emitted directly into the atmosphere, and secondary. The latter, termed as a secondary organic aerosol (SOA), is a result of oxidation of volatile organic compounds, which leads to formation of less volatile compounds that partition into the particle phase. SOA forming compounds can be classified broadly as semi- and low-volatile compounds based on their saturation vapour pressure; semi-volatile compounds reside both in the gas and particle phases in non-negligible amounts while a major fraction of low-volatile compounds can be found ultimately in the particle phase as they tend to condense irreversibly onto

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[*] Corresponding author. Tampere University of Technology, Department of Physics, P.O. Box 527, FI-33101 Tampere, Finland.
E-mail address: tatu.anttila@tut.fi (T. Anttila).

http://dx.doi.org/10.1016/j.atmosenv.2016.03.026

particles (Ehn et al., 2014; Murphy et al., 2014). The saturation vapour pressure of a SOA forming compound is a critical quantity as it influences greatly the extent of the gas/particle partitioning. This quantity has been a subject of numerous experimental and modeling studies that aim to elucidate the volatility of both individual compounds and matrix of compounds formed via oxidation processes (Hallquist et al., 2009). Using this information, together with knowledge regarding the formation mechanisms of SOA forming compounds, allows for quantifying the contribution of SOA to the regional and global aerosol loadings with large scale atmospheric models (Kanakidou et al., 2005). Such models often apply simplified theoretical frameworks for calculating the extent of gas/particle partitioning (Pankow, 1994; Odum et al., 1996; Donahue et al., 2006, 2011; Pankow and Barsanti, 2009; Cappa and Wilson, 2012), and these schemes are also used when interpreting results of experiments focusing on the volatility of SOA forming compounds (e.g. Zhao et al., 2015).

A key assumption of the afore-mentioned gas/particle partitioning models is that SOA forming compounds are in thermodynamic equilibrium with respect to the gas and the particle phases. This assumption is problematic, however, when the equilibration time is longer than a time step in a numerical model or duration of an experiment, for example. Several approaches exist, however, to estimate the time scale needed to reach the thermodynamic equilibration which can be used to assess the validity of the applied gas/particle partitioning scheme. These approaches include explicit simulation of all the physical and chemical processes involved in the mass transfer of semi-volatile compounds between the gas and aerosol phases (Shiraiwa and Seinfeld, 2012) and simplified expressions from which the equilibrium timescale can be easily calculated without involving complex numerical models (Seinfeld and Pandis, 2006).

In the current study, we derive a simplified time scale needed for a single semi- or low-volatile compound, initially residing in the gas phase, to reach thermodynamic equilibrium between the gas and particle phases. Further we show that the resulting equation combines two separate, previously derived time scales (Section 2). The validity of the expression is tested comprehensively against results from a numerical model that explicitly simulates the equilibration via condensation (Sections 3 and 4). We also discuss the limitations of the approach taken here along with the implications of the results to the experimental and numerical studies focusing on SOA formation (Section 5).

2. Characteristic times for aerosol/gas equilibrium

Let us consider mass transfer of a semi-volatile vapour i between the gas phase and a spherical particle with diameter a diameter of d_p that consists of a single, liquid-like absorbing phase (Fig. 1). According to the condensation equation (Seinfeld and Pandis, 2006), the mass transfer rate of i between the gas and the particle, J_i (moles s^{-1}), can be expressed as follows:

$$J_i = K_1 (C_{gas,i} - x_i K_2), \text{ where} \tag{1}$$

$$K_1 = 2\pi D_i d_p \beta, \text{ and } K_2 = KeC^0_{sat,i}\gamma_i = KeC_{eff,i}. \tag{2}$$

Here x_i is the mole fraction of i in the particle phase, $C_{gas,i}$ (mol m^{-3}) is the gas-phase concentration of i, MW_i (g/mol) and D_i (m^2/s) are the mole weight and gas-phase diffusion coefficient of i, respectively, β is the so-called Fuchs-Sutugin correction factor that accounts for non-continuum effects (Fuchs and Sutugin, 1971), Ke is the Kelvin term, $C^0_{sat,i}$ (mol m^{-3}) is the saturation vapour concentration of a pure compound and γ_i is the activity coefficient of i in the solution. The parameter $C_{eff,i}$ is the so-called "effective" saturation concentration that accounts for the effect of non-idealities (Donahue et al., 2011) and its value is kept constant here. Other assumptions underlying Eq. (2) are that thermodynamic equilibrium holds across the gas-particle interface, and that compound i is non-reactive, i.e. it does not participate in chemical reactions taking place in the particle phase.

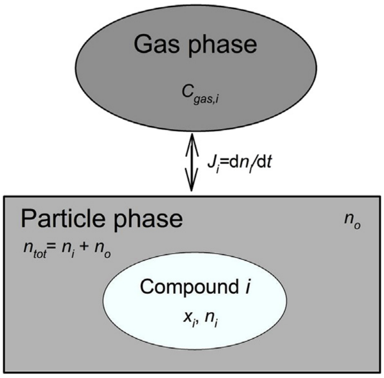

Fig. 1. Schematic figure illustrating the gas/particle partitioning of a semi-volatile compound i.

The mass transfer rate J_i, and consequently the rate at which the thermodynamic equilibrium is reached between the gas and particle phases, depends on the term ($C_{gas,i} - x_i K_2$) which also determines the direction (evaporation or condensation) of mass transfer. Here we consider equilibration via condensation and assume that the compound i is initially present only in the gas phase, i.e. $x_i(0) = 0$. It is further assumed that the particle mass does not change notably as a result of the gas/particle partitioning, i.e. the aerosol mass formed via gas/particle partitioning is relatively small compared to the initial mass of the aerosol. Consequently, the time evolution for the number of moles of i in the particle phase, n_i, due to condensation can be approximated as follows:

$$\frac{dn_i}{dt} = \frac{d(x_i \times n_{tot})}{dt} = n_{tot}\frac{dx_i}{dt} + x_i\frac{dn_{tot}}{dt} \approx n_{tot}\frac{dx_i}{dt} \tag{3}$$

where n_{tot} is the total number of moles in the particle phase. According to the assumptions made here, n_{tot} is independent of time, i.e. the total number of moles in a particle does not change notably as response to condensation of i. On the other hand, $J_i = dn_i/dt$, and Eqs. (1) and (3) can be thus combined to yield the following equation for the time evolution of x_i:

$$\frac{dx_i}{dt} = \frac{K_1}{n_{tot}}(C_{gas,i} - x_i K_2). \tag{4}$$

We further assume that the compound i has no sources in the gas phase and that condensation onto the particles forms the only sink of gaseous i. Moreover, we consider monodisperse aerosol population with a total number concentration of N_{aero} (cm^{-3}) particles. These assumptions yield the following equation for the time development of $C_{gas,i}$:

$$\frac{dC_{gas,i}}{dt} = -N_{aero}J_i. \tag{5}$$

We proceed by assuming that K_1 and K_2 do not depend on time. By differentiating Eq. (4) with respect to time and substituting Eq. (5) into the resulting equation, the following expression can be then derived for x_i: