

Mass transfer to a chemically active particle in the transition regime

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A theory of chemical uptake of gaseous reactants by aerosol particles is developed for arbitrary regimes of reactant transport. The size dependence of uptake efficiency is found for non-unity values of sticking probabilities of the reactant molecules to the particle surface. Three key points of the present consideration are:

- i. A modification of Maxwell's boundary condition for the distribution of condensing molecules over coordinates and velocities. This modified boundary condition allows accounting for the transport of reactants across the particle surface.
- ii. The solution of the collisionless Boltzmann's equation for the distribution function of reactant molecules in the free molecule zone and matching thus found concentration profile with that in the diffusion zone.
- iii. The flux conservation in the form "the reactant flux from outside = consumption of the reactant inside" is used for formulating a set of rather simple equations describing the kinetics of chemical uptake. The following processes are considered:

- i. kinetics of particle growth in absence of chemical reactions,
- ii. kinetics of uptake by a particle containing active reactant (the first and the second order kinetics)
- iii. Reactant dissociates inside the particle.

The final output of the present consideration:

- i. estimation of the characteristic times for uptake in a variety of situation,
- ii. kinetic curves (the dependence of reactant population inside the particle on time, on the sticking probability, Knudsen number etc.).

In contrast to "normal" condensation and evaporation no simple formulas exist so far describing the mass transfer to (from) a chemically active aerosol particle in the transition regime.. The attempts grounded on the numerical solution of the Boltzmann equation presented in Williams & Loyalka, 1991 are too complicated for everyday use. It is very desirable to have something similar to the Fuchs-Sutugin formula for the condensational efficiency of aerosol particles. Below we present our attempt to derive such a formula. To this end we apply the scheme developed in Lushnikov & Kulmala, 2004.

Let $J(a)$ be the mass flux onto the particle of radius a . We introduce the particle mass transfer efficiency $\gamma(a)$ as follows:

$$J(a) = \gamma(a)(n_{\infty} - n_a^+ / \beta), \quad (1)$$

Here β is the mass accommodation coefficient, a is the particle radius, and $n_a^{+\,-}$ stands for the reactant concentration above (+) or beneath (-) the particle surface. In contrast to "normal" case these concentrations are regulated by the diffusion-reaction process inside the particle and the diffusion of the reactant in the gas phase. The boundary concentrations of the reactant are linked by the Henri law $n_a^- = Hn_a^+$, with H being the dimensionless Henri constant. The efficiency $\gamma(a)$ can be expressed in terms of the diffusivity D of the gaseous reactant and the thermal velocity of the gas molecules as follows:

$$\gamma(a) = \frac{\gamma_{fm}}{1 + \beta S(av_T / 2D)}, \quad (2)$$

where $S(x) = \sqrt{1 + x^2}$ and $\gamma_{fm} = \beta\pi a^2 v_T$ is the uptake efficiency in the free-molecule regime.

Lushnikov, A.A., & Kulmala, M. (2004) *Phys. Rev. E* 70, 046413-1 – 9.

Williams, M.M.R. & Loyalka, S.K. (1991). *Aerosol Science. Theory & Practice*, Oxford, New York, Seoul, Tokyo, Pergamon P ress.