Influence of size effect on chemical reactions on surface of aerosol nanoparticles

V.V. Levdansky[1], J. Smolík[2], V. Ždímal[2] and P. Moravec[2]

[1]A.V. Luikov Heat and Mass Transfer Institute NASB, 15 P. Brovka Str., 220072 Minsk, Belarus
[2]Institute of Chemical Process Fundamentals AS CR, v.v.i., Rozvojova 135, 165 02 Prague 6, Czech Republic
Keywords: aerosol, nanoparticles, chemical reaction.
Presenting author email: vlev5@yahoo.com

Chemical reactions in aerosol systems are paramount for a number of processes occurring in the atmosphere and in various areas of chemical technology. In the case of the nanoscale aerosol particles the particle size can influence the rate of a chemical reaction on the nanoparticle surface.

The nanoparticle size can affect the activation energy of a chemical reaction (Lu and Meng, 2010) as well as the Langmuir constant for adsorption of the reactant molecules (Murzin, 2009). A decrease in the activation energy of a chemical reaction with a reduction in the nanoparticle size leads to an increase in the reactive uptake coefficient. A decrease in the Langmuir adsorption constant with a reduction in the nanoparticle size can reduce the reactive uptake coefficient. Here we consider the joint influence of the mentioned factors on the reactive uptake coefficient for the Eley-Rideal mechanism of a chemical reaction on the nanoparticle surface.

The reactive uptake coefficient γ_r for the Eley-Rideal mechanism of a chemical reaction is given by (Crowley *et al.*, 2010)

$$\gamma_r = \alpha_r \theta_B , \qquad (1)$$

where α_r is the elementary reaction probability in the collision of the gas phase reactant molecule A with the adsorbed reactant molecule B, θ_B is the surface coverage related to adsorption of molecules of the component B (for simplicity, we neglect here adsorption of molecules of the component A and the reaction product).

Taking into account the Langmuir model for adsorption and the size dependence of the Langmuir adsorption constant (Murzin, 2009), the activation energy of a chemical reaction (Lu and Meng, 2010) as well as the melting temperature and surface tension (Rekhviashvili and Kishtikova, 2006), the value of γ_r for the nanoparticle (γ_{rp}) can be written as

$$\gamma_{rp} = \alpha_{r\infty} \exp\left(\frac{4E_{r\infty}\delta}{RTd}\right) \frac{P_B K_{B\infty} \exp(-\xi)}{1 + P_B K_{B\infty} \exp(-\xi)} . \qquad (2)$$

Here $\alpha_{r\infty}$ is the value of α_r without considering the size effect, d is the particle diameter, δ is the Tolman length (it is assumed that $d >> \delta$), $E_{r\infty}$ is the activation energy of a chemical reaction on the surface of bulk matter, R is the gas constant, T is the temperature, P_B is the partial pressure of the component B in a gas phase, $K_{B\infty}$ is the Langmuir adsorption constant for adsorption of the component B on the surface of bulk matter, the value of ξ is given by

$$\xi = \frac{4\sigma_\infty V_m}{dRT}\left(1 - \frac{4\delta}{d}\right), \qquad (3)$$

where σ_∞ is the surface tension for bulk matter, V_m is the molar volume of a substance forming the nanoparticle.

Figure 1 shows the dependence of $\gamma^* = \gamma_{rp}/\gamma_{r\infty}$, where $\gamma_{r\infty}$ is the reactive uptake coefficient for bulk matter, on the dimensionless diameter $d^* = d/\delta$ at $P_B K_{B\infty}\exp(-\xi) << 1$, $\sigma_\infty V_m/(E_{r\infty}\delta) = 0.2$ and different values of the parameter $\psi = E_{r\infty}/(RT)$. It is seen that γ^* increases with a decrease in d^* and with a rise in ψ.

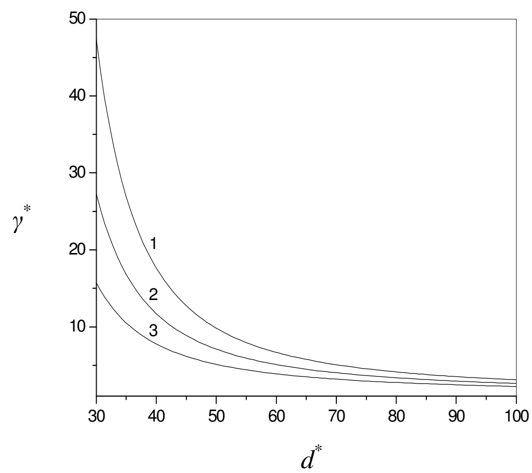

Figure 1. Dependence of γ^* on d^*; 1: $\psi = 35$, 2: $\psi = 30$, 3: $\psi = 25$.

This work was supported by GAAVCR project IAA200760905.

Crowley, J.N., Ammann, M., Cox, R.A., Hynes, R.G., Jenkin, M.E., Mellouki, A., Rossi, M.J., Troe, J. and Wallington, T.J. (2010) *Atmos. Chem. Phys.* **10**, 9059-9223.

Lu, H.M. and Meng, X.K. (2010) *J. Phys. Chem.* C **114**, 1534-1538.

Murzin, D.Yu. (2009) *Chem. Eng. Sci.* **64**, 1046-1052.

Rekhviashvili, S.Sh. and Kishtikova, E.V. (2006) *Tech. Phys. Lett.* **32**, 439-441.