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SIZE DEPENDENCE OF REACTIVE UPTAKE COEFFICIENT IN CHEMICAL REACTIONS ON AEROSOL NANOPARTICLES

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INTRODUCTION

Chemical reactions in aerosol systems play a significant role in formation of new aerosol particles and their growth in the atmosphere and in various areas of nanotechnology. In the case of nanoscale aerosol particle the size effects can sufficiently affect the rate of chemical reactions both inside the particle and on its surface. The size dependence of a chemical reaction occurring on the nanoparticle surface can be related to the size dependence of the intrinsic activation energy for a chemical reaction and the adsorption kinetics of reactant molecules. Here we consider some aspects of the possible influence of the mentioned effects on the reactive uptake coefficient in the Eley-Rideal mechanism of a chemical reaction.

RESULTS AND DISCUSSION

The reactive uptake coefficient γ_r in the Eley-Rideal mechanism of a chemical reaction can be written as (Crowley et al., 2010)

$$\gamma_{\rm r} = \alpha_{\rm r}\theta_{\rm B}, \tag{1}$$

where α_r is the elementary reaction probability in collision of a gas phase molecule A with the adsorbed molecule B, θ_B is the surface coverage by adsorbed molecules of the component B.

The value of θ_B in the Langmuir adsorption model is given by

$$\theta_{\rm B} = \frac{K_{\rm a}P_{\rm B}}{1+K_{\rm a}P_{\rm B}}, \tag{2}$$

where K_a is the Langmuir adsorption equilibrium constant, P_B is the partial pressure of molecules of the component B in a gas phase (for simplicity we neglect here adsorption of molecules of the component A and the reaction product).

The reactive uptake coefficient depends on the nanoparticle size due to the size dependence of K_a (Murzin, 2009) and the size dependence of α_r. Taking into account the dependence of α_r for the nanoparticle on the activation energy of a chemical reaction for the nanoparticle E_{rp}, assuming that E_{rp} is related to the activation energy for a heterogeneous chemical reaction for bulk matter $E_{r\infty}$ analogously to the equation for the activation energies for different processes that is given by Vanithakumari and Nanda (2008) and using the size dependence of the nanoparticle melting temperature according to Rekhviashvili and Kishtikova (2006), the value of γ_r for nanoparticle (γ_{rp}) in K_aP_B <<1 and d/δ >>1, where d is the diameter of the nanoparticle and δ is the Tolman length, can be written as

$$\gamma_{\text{rp}} = \alpha_{\text{r}\infty} K_{\text{a}\infty} P_{\text{B}} \exp\left[\frac{4E_{\text{r}\infty}}{RTd^*}\left(1 - \frac{\sigma V_{\text{m}}}{E_{\text{r}\infty}\delta}\right)\right], \quad (3)$$

where $\alpha_{r\infty}$ and $K_{a\infty}$ are respectively the reaction probability and Langmuir adsorption constant for bulk matter, R is the gas constant, T is the temperature, V_m is the molar volume for the substance forming the nanoparticle, σ is surface tension (it is assumed to be size-independent), $d^* = d/\delta$.

Figure 1 shows the dependence of $\gamma^* = \gamma_{rp}/(\alpha_{r\infty}K_{a\infty}P_B)$ on d^* at different values of parameters $\varphi = \sigma V_m/(E_{r\infty}\delta)$ and $\psi = E_{r\infty}/(RT)$.

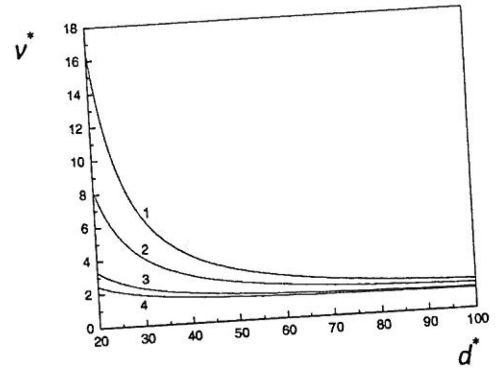

Fig. 1. Dependence of γ^* on d^*; 1, 2: $\varphi = 0.3$; 3, 4: $\varphi = 0.7$; 1, 3: $\psi = 20$; 2, 4: $\psi = 15$.

CONCLUSIONS

Thus, it is shown that the value of γ^* for the aerosol nanoparticle is affected by the size dependence of the Langmuir adsorption constant and the activation energy of a chemical reaction. The value of γ^* increases with a decrease in the nanoparticle size.

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REFERENCES

Crowley J.N., Ammann M., Cox R.A., Hynes R.G., Jenkin M.E., Mellouki A., Rossi M.J., Troe J., Wallington T.J., Evaluated kinetic and photochemical data for atmospheric chemistry: Volume V – heterogeneous reactions on solid substrates, *Atmos. Chem. Phys.*, 10, 9059–9223 (2010).

Murzin D.Yu., Thermodynamic analysis of nanoparticle size effect on catalytic kinetics, *Chem. Eng. Sci.*, 64, 1046–1052 (2009).

Rekhviashvili S.Sh., Kishtikova E.V., On the temperature of melting of nanoparticles and nanocrystalline substances, *Tech. Phys. Lett.*, 32, 439–441 (2006).

Vanithakumari S.C., Nanda K.K., A universal relation for the cohesive energy of nanoparticles, *Phys. Lett. A*, 372, 6930–6934 (2008).