Size-Dependent Rate Constant of Chemical Reactions in Nanoscale Particles

Levdansky, V.V.
2011

SIZE-DEPENDENT RATE CONSTANT OF CHEMICAL REACTIONS IN NANOSCALE PARTICLES

Valeri LEVDANSKY[1,2], Jiří SMOLÍK[2], Vladimír ŽDÍMAL[2], Pavel MORAVEC[2]

[1]Heat and Mass Transfer Institute NASB, Minsk, Belarus, email: vlev5@yahoo.com
[2]Institute of Chemical Process Fundamentals AS CR, v.v.i., Prague, Czech Republic

Keywords: Size effect, Nanoparticles, Chemical reactions

INTRODUCTION

It is known that many processes occurring in heterogeneous systems with nanoscale objects are characterized by some specific features due to size dependence of parameters describing processes in question. This can in particular affect nanoparticle formation. Some problems related to the trapping of impurity molecules by nanoparticles were considered in (Levdansky et al., 2009). Here we study the influence of the size effect on chemical reactions inside nanoparticles.

RESULTS AND DISCUSSION

Let us consider the size dependence of chemical reaction occurring in the nanoscale particle. The rate of bimolecular chemical reaction *j* can be written as (Keizer, 1987)

$$j = k^{*} n_{\mathrm{A}} n_{\mathrm{B}}, \qquad (1)$$

where n_A and n_B are the number densities of reactants A and B, k^* is the effective rate constant for bimolecular chemical reaction that is given by

$$k^{*} = \frac{k_{\mathrm{d}} k_{\mathrm{r}}}{k_{\mathrm{d}} + k_{\mathrm{r}}}, \qquad (2)$$

where $k_d=4\pi DR_0$, D is the sum of the diffusion coefficients D_A and D_B for the components A and B, R_0 is the effective radius at which the reaction can occur, k_r is the rate constant for intrinsic bimolecular chemical reaction (without the diffusion effect).

The values of D and k_r for nanoparticle D_p and k_{rp} are given by

$$D_{\mathrm{p}} = D'_{\mathrm{Ap}} \exp\left(-\frac{E_{\mathrm{dAp}}(d)}{kT}\right) + D'_{\mathrm{Bp}} \exp\left(-\frac{E_{\mathrm{dBp}}(d)}{kT}\right), \qquad (3)$$

$$k_{\mathrm{rp}} = k'_{\mathrm{rp}} \exp\left(-\frac{E_{\mathrm{rp}}(d)}{kT}\right). \qquad (4)$$

Here k is the Boltzmann constant, T is the temperature, E_{dAp} and E_{dBp} are the activation energies for diffusion of components A and B in the nanoscale particle, E_{rp} is the activation energy for intrinsic bimolecular chemical reaction in the nanoparticle. Pre-exponential factors D'_{Ap}, D'_{Bp} and k'_{rp} are assumed further for simplicity to be constant and equal to the values for a bulk matter.

The influence of the size effect on the value of D_p is related to a decrease in the activation energy for diffusion of reactants with a reduction in the particle size due to size dependence of the cohesive energy (Vanithakumari and Nanda, 2008). It leads to an increase in the value of k_d.

A decrease in the cohesive energy in the nanoscale particle with a reduction in its size can lead also to an increase in k_{rp}.

Taking into account the relation between the activation energy for diffusion of components in small particles and their melting temperature by analogy with (Vanithakumari and Nanda, 2008) and allowing for size dependence of the melting temperature according to (Rekhviashvili and Kishtikova, 2006), we can obtain equation for the size-dependent rate constant of chemical reaction in the nanoscale particle. Figure 1 shows the dependence of the dimensionless rate constant of chemical reaction for the diffusion controlled regime $k^{*}=k_{dp}/k_{d\infty}$, were $k_{d\infty}$ is the value of k_d without considering the size effect, on the dimensionless particle diameter $d^{*}=d/\delta$, were d is the particle diameter, δ is the Tolman length. For simplicity we assume that $E_{dAp}=E_{dBp}$ (e.g., such condition takes place in recombination of atoms inside the nanoparticle). It is seen from Fig. 1 that k^{*} increases with a decrease in the particle size.

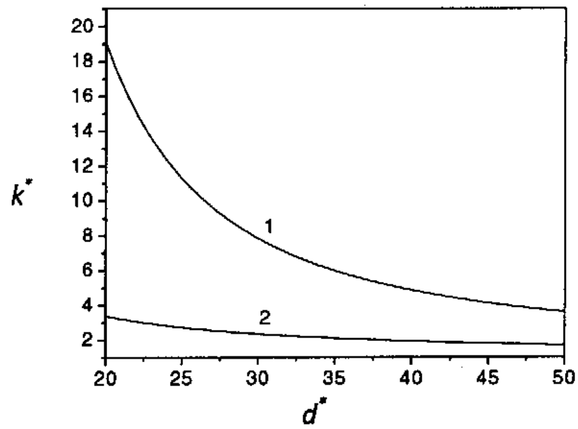

Fig. 1: Dependence of k^{*} on d^{*} in the diffusion controlled regime of chemical reaction; 1: $E_{d\infty}/kT$= 17, 2: $E_{d\infty}/kT$=7, $E_{d\infty}$ is the activation energy for diffusion of reactant molecules in a bulk matter.

CONCLUSIONS

Thus, it is shown that the influence of the size effect on chemical reactions in nanoscale particles can be related to a dependence of the activation energies for diffusion of atoms (molecules) in the nanoparticle and for intrinsic chemical reaction on the particle size.

ACKNOWLEDGEMENTS

This work was supported by GA AV CR projects IAA400720804, IAA200760905 and GACR project 101/09/1633.

REFERENCES

Keizer J. (1987) Diffusion effects on rapid bimolecular chemical reactions, *Chem. Rev.* **87**, 167-180.

Levdansky V.V., Smolík J., Moravec P. (2009) Impurity Trapping by Aerosol Particles, *Aerosol Air Quality Res.* **9**, 257-265.

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

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