Impurity Trapping by Aerosol Particles

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Abstract

The trapping of foreign gas molecules (atoms) by growing aerosol particles as well as by already formed particles is considered. The trapping coefficients are obtained for both above-mentioned cases. The influence of size effect on the trapping coefficient is discussed.

Keywords: Aerosol particles; Impurity; Trapping coefficient.

INTRODUCTION

The problems related to formation of nanosized aerosol particles are of principal interest for both processes of modern technology, e.g. manufacture of fine particles (Davis, 2001) and different kinds of atmospheric processes, e.g. formation of water drops (Seinfeld and Pandis, 2006). The trapping of impurity gas molecules (atoms) by aerosol particles is one of the above-mentioned problems. It is well known that even very small concentration of impurity molecules in the condensed phase can substantially change certain physicochemical properties of the product. The control of the impurity molecule concentration in the substance is of paramount significance in particular in the production of microelectronics elements. In some cases, it is necessary to remove impurities from a gas phase. This can be achieved by trapping of impurity molecules by aerosol particles followed by removal of aerosol particles from the gas phase. The trapping of impurity molecules in condensational growth of aerosol particles is closely related to cryotrapping widely used in the cryogenic technology for pumping out molecules of noncondensable components by condensation of easy condensing components (Minaichev, 1978). Further, we shall consider the trapping of impurity molecules (atoms) by growing aerosol particles and also by already formed nanoparticles.

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MOLECULE TRAPPING BY VAPOR CONDENSATION ON AEROSOL PARTICLE

Trapping of non-condensable molecules by growing aerosol particle is a special case of substance deposition from a gaseous mixture on the particle surface. To solve this problem it is necessary to know the resulting molecular fluxes of individual species onto the particle. These fluxes are obtained as a difference between the condensation fluxes of components into the particle and evaporation fluxes from it. The flux of molecules of given species, striking the particle, depends on partial vapor pressure of the substance in question. The evaporation flux of the substance from the surface depends on equilibrium vapor pressure of the substance at surface temperature that further depends on concentration of components in the condensed phase. These concentrations, in turn, depend on the component concentrations in the gas. Thus, the problem of calculation of impurity concentration in the particle should be analysed simultaneously with the problem of concentration determination of individual gaseous species near the particle surface.

There are two approaches usually used to determine component concentrations in the condensed phase. In the first one the equation valid only for equilibrium conditions are used, where numbers of evaporating and condensing molecules are equal. The second approach is based on the other limiting case, when evaporation of components from the condensate is not allowed at all. But real

conditions can lie between these limiting cases. It should be noted that deposition processes in modern technology often take place in the regime very far from equilibrium (e.g., in deposition of thin films or in preparation of nanoparticles).

All the foregoing leads to the conclusion that the description of the impurity molecule trapping by growing aerosol particles requires the model of substance deposition from a gaseous mixture on the aerosol particle surface which should be valid for highly non-equilibrium conditions and should account for trapping of molecules of non-condensable components by growing particles. In the general case it should also allow describing the deposition process for arbitrary Knudsen number Kn, defined as the ratio of mean free path of gas molecules to the particle radius, and include the influence of the density of the resulting flux of vapor molecules onto the particle (and respectively the particle growth rate) on the trapping of impurity molecules. Further for simplicity we shall consider the case of the free-molecule regime of gas flow (Kn >> 1).

Here we consider the trapping of impurity molecules by vapor condensation on the surface of the aerosol particle on the basis of a single-stage model of substance deposition in which the molecules of a gas are assumed to enter directly to the condensed phase (the processes related to the surface structure and transport of impurity molecules over the surface and in the condensed phase are not considered, the relative concentration of the components on the surface and in its volume

are assumed to be equal). It is worth noting that in more detailed description of the trapping process one should use a model which takes account of the possibility for the presence of a different number of bonds of an impurity molecule with the molecules of the basic component (similarly to the model used to describe crystal growth which considers the migration of molecules (atoms) over the surface and their imbedding into the steps and terraces existing on the surface). Taking into account above-mentioned assumptions relative concentration of impurity molecules in the condensed phase c_2 can be connected with the resulting flux densities of vapor (J_1) and impurity (J_2) molecules onto the condensed phase (we will further indicate the values related to the vapor by index 1 and related to the impurity component by index 2)

$$c_2 = \frac{J_2}{J_1 + J_2} \tag{1}$$

The density of the resulting flux of impurity molecules entering the particle J_2 is equal to a difference between the flux density of impurity molecules that stick to the particle and the flux density of molecules that evaporate from the particle. The value of J_2 can be written in the form (Levdansky, 1979; Levdansky et al., 2000)

$$J_2 = \beta N_2 - \frac{J_2}{J_1 + J_2} F_2 \tag{2}$$

Here β is the sticking coefficient of impurity molecules, N_2 is the flux density of impurity

molecules incident on the surface. The value of F_2 is given by

$$F_2 = n_c \left(\frac{kT}{2\pi m_2} \right)^{1/2} \exp\left\{ -\frac{Q_2}{kT} \right\} \tag{3}$$

where n_c is the total number density of molecules in the condensed phase assumed to be constant (this assumption is carried out when sizes of vapor and impurity molecules are cloze), Q_2 is the evaporation energy of impurity molecule, k is the Boltzmann constant, T is the temperature, m_2 is the mass of the impurity molecule. It is worth noting that the flux density of impurity molecules that evaporate from the particle is equal to $c_2 F_2$.

The value of N_2 under an assumption of the Maxwell velocity distribution function for gas molecules can be presented as $n_2 v_2 / 4$, where n_2 and v_2 are correspondingly the number density of impurity molecules in the gas phase and the mean velocity of these molecules. Taking into account Eq. (2) in the case of $J_2 \ll J_1$ we can write in quasi-stationary approximation following equations for the relative concentration of impurity molecules c_2 and the trapping coefficient of impurity molecules γ which is determined as the ratio of the density of the resulting flux of impurity molecules into the condensed phase to the density of the flux of impurity molecules incident on the particle surface ($\gamma = J_2 / N_2$)

$$c_2 = \frac{\beta N_2}{J_1 + F_2} \tag{4}$$

$$\gamma = \frac{\beta J_1}{J_1 + F_2} \tag{5}$$

It should be noted that Eqs. (4) and (5) can be obtained from Eqs. (1) and (2) in neglecting terms proportional to J_2^2.
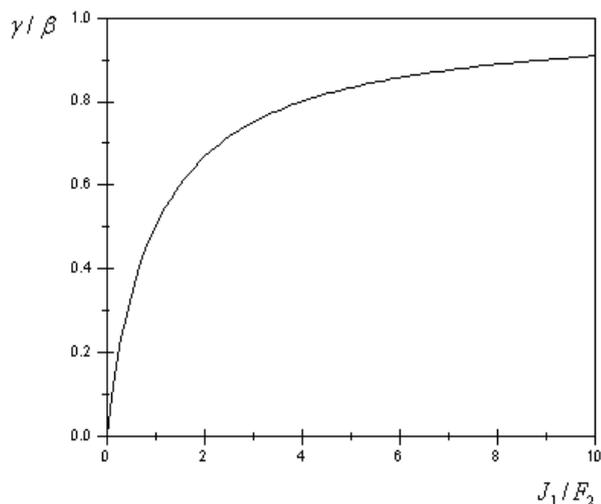

Fig. 1. Dependence of the relative trapping coefficient γ / β on the dimensionless resulting flux of the condensable component J_1 / F_2.
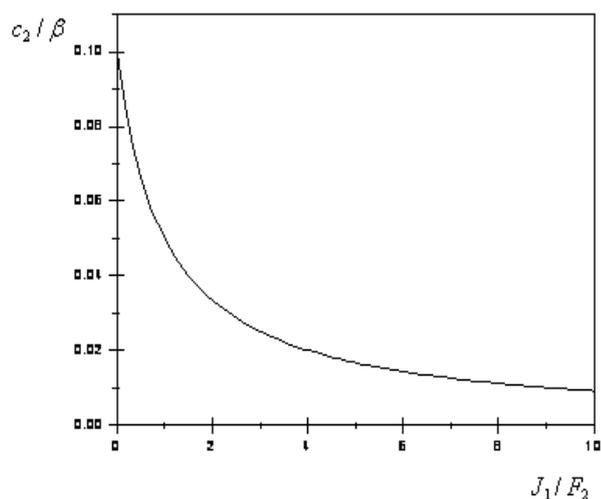

Fig. 2. Dependence of the value c_2 / β on the dimensionless resulting flux of the condensable component J_1 / F_2 at. $N_2 / F_2 = 0$.

Figs. 1 and 2 show respectively the dependence of the values γ / c and c_2 / β on the relative resulting flux of the condensable component J_1 / F_2 (and accordingly on the particle growth rate). It follows from these figures that with the increase of J_1, with the rest of parameters being constant, the trapping coefficient increases and the concentration of impurity component decreases. It is connected with the fact that with the increase in the condensation rate the probability for the impurity molecules to be trapped by the growing particle increases but the number of molecules of the basic component per each impurity molecule trapped by the condensed phase is also increased (the last factor leads to the decrease in the relative concentration of impurity molecules with the rise of the growth rate of the particle).

In the case of sufficiently small aerosol particle, when the Kelvin effect influences evaporation of the particle, the value of J_1 in the free-molecular flow regime in view of (Seinfeld and Pandis, 2006) can be written as (further we consider for simplicity the isothermal case)

$$J_1 = \frac{\alpha v_1}{4}\left[n_1 - n_{1e} \exp\left(\frac{4\sigma V_m}{dkT} \right) \right] \tag{6}$$

where α is the condensation coefficient (that is assumed to be equal to the evaporation coefficient), v_1 is the mean velocity of vapor molecules, n_1 is the number density of the vapor molecules, n_{1e} is the number density of molecules of the saturated vapor for a flat surface, σ is surface tension, d is the particle

diameter , $V_m V_m$ is the volume per molecule in the particle.

It is seen from Eqs. (5) and (6) that with a decrease of the particle size the trapping coefficient will decrease (a possible decrease of the sticking coefficient and the evaporation energy of impurity molecules with the decrease of the particle size also leads to a decrease of the trapping coefficient). Eq. (5) shows that the probability of the impurity molecule trapping by the growing aerosol particle and hence the resulting flux density of the impurity molecules into the particle is greater than zero if $J_1 > 0$ and $\beta > 0$. This leads to the trapping of the noncodensable component of a gas phase in condensation of a vapor. In particular this effect can lead to the trapping of molecules of a buffer gas by growing clusters in the process of homogeneous nucleation. It should be noted that values of γ and c_2 can change under influence of resonance (e.g. laser) radiation that is related to a change in the resonance radiation field of β and Q_2 .

It is worth noting that in the case when heterogeneous nucleation of one component of gas mixture takes place on the aerosol particle surface the trapping of impurity molecules can occur on the gas-embryo interface (similarly to the above-considered model) and on the triple-interface boundary between gas, embryo and substrate. The last process depends sufficiently on surface diffusion of impurity molecules along the surfaces of the embryo and the substrate. The effective trapping coefficient in the case of heterogeneous nucleation is affected by both above-mentioned processes.

TRAPPING OF IMPURITY ATOMS BY FORMED NANOSCALE PARTICLES

Let us consider the trapping (absorption) of impurity atoms by formed nanosized aerosol particles in the free molecular regime of gas flow. This process will be illustrated by the example of the trapping of Ag atoms by Ir nanoparticles. We shall use the two-stage model for atom transition from a gas phase into nanoparticles related to adsorption of gas atoms on the particle surface with subsequent transition to the absorbed state. The size effect in this case can be related in particular to a change of the activation energy for transition of adsorbed atoms to the absorbed state with a decrease of the particle size. A change of the mentioned activation energy is due to greater concentration of vacancies in the nanoparticle than in the bulk substance that is related to a decrease of the vacancy formation energy in small particles (Qi and Wang, 2004; Gladkikh *et al.*, 2004). The nanoparticles are more "friable (porous)" than the bulk substance that leads to a higher probability for transition of the adsorbed atom onto the small particle (adsorbed state) in comparison with the bulk substance. Concentrations of both adsorbed and absorbed impurity atoms are assumed further to be sufficiently small. Taking into account above-mentioned, we can write, according to (Nathanson *et al.*, 1996), following equations connecting number densities of atoms in the

gas (n_g) and adsorbed (n_a) phases for the initial stage of the absorption process:

$$\gamma \frac{n_g v}{4} = \beta \frac{n_g v}{4} - n_a k_g \qquad (7)$$

$$\gamma \frac{n_g v}{4} = n_a k_c \qquad (8)$$

where k_g and k_c are respectively the rate constants of atom transitions from the adsorbed phase to the gas and the condensed phase (absorbed state) that can be written as

$$k_g = k_g' \exp\left(-\frac{Q_g}{kT}\right) \qquad (9)$$

$$k_c = k_c' \exp\left(-\frac{Q_c}{kT}\right) \qquad (10)$$

Here Q_g and Q_c are respectively activation energies for transitions of adsorbed atoms into the gas (desorption) and their transfer into the condensed phase (absorption), v is the mean velocity of atoms in the gas phase. Pre-exponential factors k_g' and k_c' are assumed further to be constant. The trapping coefficient of atoms by the formed aerosol particle γ is defined similar to the case of condensational growth of the particle.

It is worth noting that the right-hand side of Eq. (7) similarly to the right-hand side of Eq. (2) describes a difference in the flux densities of molecules that stick to the particle and evaporate from it. Distinction consists that in the first case (Eq. (2)) the resulting flux density of foreign gas molecules onto the particle depends on the resulting flux density of the vapor molecules and respectively on the particle growth rate.

Taking into account Eqs. (7)-(10), we can obtain following equation for the trapping coefficient for atoms:

$$\gamma = \frac{\beta}{1 + \dfrac{k_g}{k_c}} = \frac{\beta}{1 + \dfrac{k_g'}{k_c'} \exp\left(-\dfrac{Q_g - Q_c}{kT}\right)} \qquad (11)$$

Let us assume that $k_g' = k_c'$ In the case when $Q_c > Q_g$ and $\exp\{(Q_c - Q_g)/kT\} \gg 1$ (these conditions usually take place) the value of γ is given by

$$\gamma = \beta \exp\left(-\frac{Q_c - Q_g}{kT}\right) \qquad (12)$$

It is known that nanosized particles are characterized by lower value of melting temperature than the bulk substance. The activation energy for diffusion of atoms in the nanosized particle E_p in accordance with (Jiang et al., 2004) can be presented as

$$E_p = E_\infty \frac{T_{mp}}{T_{m\infty}} \qquad (13)$$

where T_{mp} is the melting temperature for the small particle, E_∞ and $T_{m\infty}$ are respectively the activation energy for diffusion of atoms in the bulk substance and the melting temperature of the bulk substance.

Let us suppose that in the case of the small particle the equation similar to Eq. (13) can be written

$$Q_{cp} = Q_{c\infty} \frac{T_{mp}}{T_{m\infty}} \qquad (14)$$

where $Q_{c\infty}$ and Q_{cp} are respectively activation energies for absorption of atoms in the case of the bulk substance and the small particle.

The dependence of T_{mp} on the particle diameter according to (Rekhviashvili and Kishtikova, 2006) can be presented as

$$T_{mp} = T_{m\infty} \exp\left(-\frac{4\delta}{\delta + d}\right) \qquad (15)$$

where δ is Tolman's length that according to (Tolman, 1949) can change for different substances from 0.096 to 0.35 nm.

Taking into account above-stated the value of γ is given by

$$\gamma = \beta \exp\left\{-\frac{Q_{c\infty}}{kT}\left[\exp\left(-\frac{4\delta}{\delta + d}\right)\right] + \frac{Q_g}{kT}\right\} \qquad (16)$$

The relative trapping coefficient $\bar{\gamma} = \gamma / \gamma|_{d\to\infty}$ under assumption that β and Q_g are independent of the particle size is given by

$$\bar{\gamma} = \exp\left\{\frac{Q_{c\infty}}{kT}\left[1 - \exp\left(-\frac{4\delta}{\delta + d}\right)\right]\right\} \qquad (17)$$

Fig. 3 shows dependence of the relative trapping coefficient $\bar{\gamma}$ on the dimensionless particle diameter $\bar{d} = d / \delta$ for the trapping of Ag atoms by Ir nanoparticles. In this case the value of Q_g for low concentration of adsorbed atoms of Ag is equal to 3.7 eV and the lowest value of $Q_{c\infty}$ can be estimated as 5 eV (Gall *at al.*, 2004).

It is seen from Fig. 3 that the value of $\bar{\gamma}$ increases with the decrease of the particle size. It is worth noting that the real dependence of the trapping coefficient on the particle size can be more complicated due to a possible dependence of β and Q_g on the size of the particle. It is pertinent to note that the increase of the mobility of foreign atoms in small particles due to the rise of vacancy concentration in the particle can lead to the
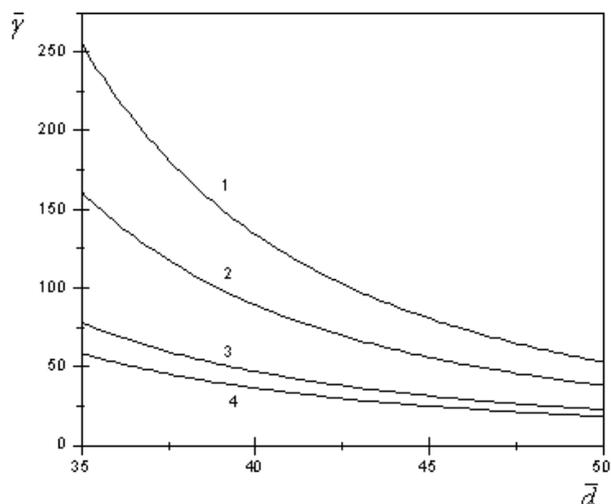

Fig. 3. Dependence of the relative trapping coefficient $\bar{\gamma} = \gamma / \gamma|_{d\to\infty}$ on the dimensionless particle diameter $\bar{d} = d / \delta$ in the trapping of Ag atoms by Ir nanoparticles at $Q_{c\infty} = 5$ eV: $1 - T = 1100$ K, $2 - T = 1200$ K, $3 - T = 1400$ K, $4 - T = 1500$ K.

increase of the rate of formation of clusters from above mentioned atoms in nanoparticles in comparison with the bulk substance.

It should be noted that above we considered only some specific features affecting the trapping coefficient of molecules (atoms) by small aerosol particles that related to particle growth and the size effects. In the general case the trapping of impurity molecules by nanoparticles depends on the joint influence of mass transfer of impurity molecules to the particle surface in the gas phase and in the particle itself and also on surface processes on the particle-gas interface.

CONCLUSIONS

The trapping of molecules (atoms) by growing aerosol particles and by already formed nanoscale particles has been analyzed. It is shown that the trapping of impurity molecules by growing aerosol particle increases with the increase of the resulting flux of vapor molecules into the particle. The increase of the trapping coefficient of atoms by the formed nanoscale particle with the decrease of its size can be related to the decrease of the activation energy for transition of impurity atoms from the adsorbed to absorbed state with the reduction of the particle size.

ACKNOWLEDGMENTS

REFERENCES

Davies, R. (2001). Particle Science and Technology-a View at the Millennium. *Powder Technology.* 119: 45-57.

Gall, N.R., Rut'kov, E.V. and Tontegode, A.Y. (2004). Interaction of Silver Atoms with Iridium and Two-dimensional Carbon Film on Iridium: Adsorption, Desorption, Solution. *Fiz. Tv. Tela.* 46: 360-366.

Gladkikh, N.T., Dukarov, S.V., Kryshtal, A.P., Larin, V.I., Sukhov, V.N. and Bogatyrenko, S.I. (2004). Surface Phenomena and Phase Transitions in Condensed Films. V.N. Karazin Kharkov National University, Kharkov.

Jiang, Q., Zhang, S.H. and Li, J.C. (2004). Grain Size-dependent Diffusion Activation eEnergy in Nanomaterials. *Solid State Commun.* 130: 581-584.

Levdansky, V.V. (1979). Kinetics of Substance Precipitation from a Gas Mixture. *J. Eng. Phys.* 37: 1145-1150.

Levdansky, V.V., Smolik, J. and Moravec, P. (2000). Trapping of Impurity Molecules in Condensation from Mixtures of Gases. *Int. J. Heat Mass Transfer.* 43: 629-637.

Minaichev, V.E. (1978). *Vacuum Cryopumps*: Energiya, Moscow.

Nathanson, G.M., Davidovits, P., Worsnop, D.R. and Kolb, C.E. (1996). Dynamics and Kinetics at the Gas-liquid Interface. *J. Phys. Chem.* 100: 13007-13020.

Qi, W.H. and Wang, M.P. (2004). Vacancy Formation Energy in Small Particles. *J. Mater. Sci.* 39: 2529-2530.

Rekhviashvili, S. and Kishtikova, E. (2006).

On the Temperature of Melting of Nanoparticles and Nanocrystalline Substances. *Tech. Phys. Lett*. 32: 439-441.

Seinfeld, J.H. and Pandis, S.N. (2006). *Atmospheric Chemistry and Physics*: *From Air Pollution to Climate Change*, John Wiley & Sons, Inc., New York.

Tolman, R.C**.** (1949). The Effect of Droplet Size on Surface Tension. *J. Chem. Phys*. 17: 333-337.