

Monte Carlo Simulation Of Heterogeneous Catalytic Processes On Heat Shield Coatings Of Space Vehicles

V.L. Kovalev, V. Ju. Sazonova and A.N. Jakunchikov

*Mechanics and Mathematics Faculty, Moscow State University named after M.V. Lomonosov,
119992, Leninskie Gory, Moscow, Russia*

Abstract. Numerical method for Monte Carlo simulation of the heterogeneous catalytic atomic recombination has been developed. It makes possible to account all elementary steps involved in the surface atomic recombination. Calculated adsorbed atom concentrations and heterogeneous catalytic atom recombination probability agrees well with known analytical and numerical solutions and experimental data. Thus, this method may be used to simulate the heterogeneous catalytic atom recombination on heat shield coatings of space vehicles.

Keywords: Monte Carlo simulation, heterogeneous catalytic processes, space vehicles coatings.

PACS: 02.70.Uu, 82.65.-s

INTRODUCTION

Studying of the heterogeneous atom recombination is an actual problem for many applications. For example, characteristics of plasma reactors, aerodynamic heating of reusable vehicles and pollution of satellite surface on high altitudes essentially depend on surface processes [1-6].

A lot of study has been carried out last years with the purpose of physical understanding of elementary processes which occur on a surface. Usually, heterogeneous catalytic processes are considered in the determined formulation, when concentrations of adsorbed particles represent the continuous functions satisfying the differential equations. These balance equations follow from conservation laws. However, in some cases the microscopic approach is necessary, for example at the account of a spatial arrangement of adsorbed particles in a crystal lattice. This paper follows dynamic Monte Carlo method [3, 5], in which a relationship between Monte Carlo time and real time is clearly established. This method is applied for dissociated air recombination on the catalytic surface and comparisons of calculated and experimental values of the atom recombination probability were made.

DYNAMICAL MONTE CARLO METHOD

The surface was represented as a matrix of the large dimension which cells are the active centers for physical and for chemical adsorption. It was supposed, that adsorbents originally are absent on a surface.

Cell selection was made by random choice, and properties of the cell were analyzed further. The cell can be occupied or free, intended for physical or chemical adsorption depending on probabilities of possible processes on this cell. The hierarchy of elementary process probabilities was under construction on rate values of these processes on each cell type. With its help it was determined, what from processes should take place by the next random selection of a cell not to break a proper correlation between occurring reactions and their rates.

The correspondence of system positions with real time was established the next way. We shall designate relative probability i -th process through $p_i \in [0,1]$. These characteristics depend directly on reaction average speed values. If only one process corresponds to each cell type, then p_i can be chosen as $p_i = r_i / \lambda_{\max}$, $\lambda_{\max} = \max(r_i)$. If k reactions with rates r_i ($i = 1, \dots, k$) can occur on a cell, then process

probabilities can be chosen as $p_i = r_i / \lambda_{\max}$, $\lambda_{\max} = \max(r_1 + \dots + r_k)$. Here value λ_{\max} was searched for all cell types.

The probability hierarchy gives a required ratio between quantities of the different types of processes. Let's notice, that $r_i dt$ processes of i -th type occur on one active center for dt period. The total quantities of i -th type processes, occurred on investigated surface segment are $N_i = (r_i dt) S_i$. Here S_i are active center quantities of surface segment on which this process occurs. Thus quantities of the various processes, which have occurred on this surface segment, submit to a ratio

$$N_1 : N_2 : \dots : N_R = r_1 S_1 : r_2 S_2 : \dots : r_R S_R, \text{ or } N_1 : N_2 : \dots : N_R = p_1 S_1 : p_2 S_2 : \dots : p_R S_R. \quad (1)$$

It was supposed, that there is only one process on any cell. After any process time value increases by adding of an increment Δt , which was chosen as $\Delta t = \frac{1}{\Omega}$. Here $\Omega = \sum_i r_i S_i$. We note, that the

value of processes which occurs for a real time interval dt is $\left(\sum_i r_i S_i \right) dt$. The algorithm operating time interval corresponds to a real time interval by such a selection Δt . Really, the ratio (1) gives, if $r_1 S_1 \tau$ processes of the first type have taken place for an interval of real time τ , then $r_i S_i \tau$ processes of i -th type have taken place for this interval of real time. Thus the operating time has changed to

$$\Delta T = \Delta t (r_1 S_1 \tau + r_2 S_2 \tau + \dots) = \frac{(r_1 S_1 + r_2 S_2 + \dots)}{\Omega} \tau = \tau.$$

KINETIC MODEL OF HETEROGENEOUS CATALYTIC RECOMBINATION

Chemically and physically adsorbed atoms were taken into account during catalytic heterogeneous recombination of dissociated air. The reaction mechanism included physical and chemical adsorption of atoms, surface diffusion of physisorbed atoms and recombination of adsorbed atoms in Eley – Riddle and Langmuir-Hinshelwood reactions.

1. $N + F_v \rightarrow N_F$, 2. $N_F \rightarrow N + F_v$, 3. $N + S_v \rightarrow N_s$, 4. $N + N_s \rightarrow N_2 + S_v$, 5. $N_F + S_v \rightarrow N_s + F_v$,
6. $N_F + N_s \rightarrow N_2 + F_v + S_v$, 7. $O + F_v \rightarrow O_F$, 8. $O_F \rightarrow O + F_v$, 9. $O + S_v \rightarrow O_s$, 10. $O + O_s \rightarrow O_2 + S_v$,
11. $O_F + S_v \rightarrow O_s + F_v$, 12. $O_F + O_s \rightarrow O_2 + F_v + S_v$.

Here F_v and S_v are vacant sites for physical and chemical adsorption correspondingly; N_F , N_s and O_F , O_s are physisorbed and chemisorbed nitrogen and oxygen atoms correspondingly.

In case of nitrogen atom recombination only, the rates of species formation in heterogeneous catalytic reactions are

$$R_1 = k_1 [N] (1 - \theta_F^N) [F], \quad R_2 = k_2 \theta_F^N [F], \quad R_3 = k_3 [N] (1 - \theta_s^N) [S], \quad R_4 = k_4 [N] \theta_s^N [S],$$

$$R_5 = k_5 [S] [F] \theta_F^N (1 - \theta_s^N), \quad R_6 = k_6 \theta_F^N \theta_s^N [F] [S].$$

Here $[N]$ is gas phase concentration of nitrogen atoms.

Total densities of sites for physical adsorption $[F]$ and chemical adsorption $[S]$, physically adsorbed atom concentrations θ_F^N and chemically adsorbed atom concentrations θ_s^N are expressed as follows

$$[F] = [F_v] + [N_F], \quad [S] = [S_v] + [N_s], \quad \theta_F^N = [N_F] / [F], \quad \theta_s^N = [N_s] / [S].$$

Hence, θ_F^N and θ_s^N satisfy the system of differential equations

$$\frac{d\theta_F^N}{dt} = (1 - \theta_F^N) [N] k_1 - \theta_F^N k_2 - \theta_F^N (1 - \theta_s^N) [S] k_5 - \theta_F^N \theta_s^N [S] k_6 \quad (2)$$

$$\frac{d\theta_s^N}{dt} = (1 - \theta_s^N)[N]k_3 - \theta_s^N[N]k_4 + \theta_F^N(1 - \theta_s^N)[F]k_5 - \theta_F^N\theta_s^N[F]k_6 \quad (3)$$

The data [1-5] were used for elementary stages rate coefficients. Thus it was supposed, that typical radius of an adsorption site $a \sim 10^{-8}$ cm, $[F]=10^{16}$ cm $^{-2}$ and $[S] / [F]=2 \times 10^{-3}$.

One can obtain the analytical solution (2), (3), if reactions 5 and 6 are not taken into account. So, if at $t = 0$ we have $\theta_F^N = \theta_s^N = 0$, then

$$\theta_F^N(t) = \frac{r_1^N}{r_1^N + r_2^N} \left(1 - e^{-(r_1^N + r_2^N)t} \right), \quad \theta_s^N(t) = \frac{r_3^N}{r_3^N + r_4^N} \left(1 - e^{-(r_3^N + r_4^N)t} \right) \quad (4)$$

Here $r_1^N = [N]k_1$, $r_2^N = k_2$, $r_3^N = [N]k_3$, $r_4^N = [N]k_4$ mean populate and depopulate rates.

COMPARISON MONTE CARLO RESULTS WITH THEORETICAL AND EXPERIMENTAL DATA

First, the Monte –Carlo solution were tested with analytical solution (4). Comparison calculated concentrations θ_F^N and θ_s^N with analytical solution (4) show good agreement in the same assumptions. The good consent of the calculated values of the adsorbed atom concentration is observed with Monte Carlo solution [5] when reactions 5 and 6 are taken into account (Fig.1).

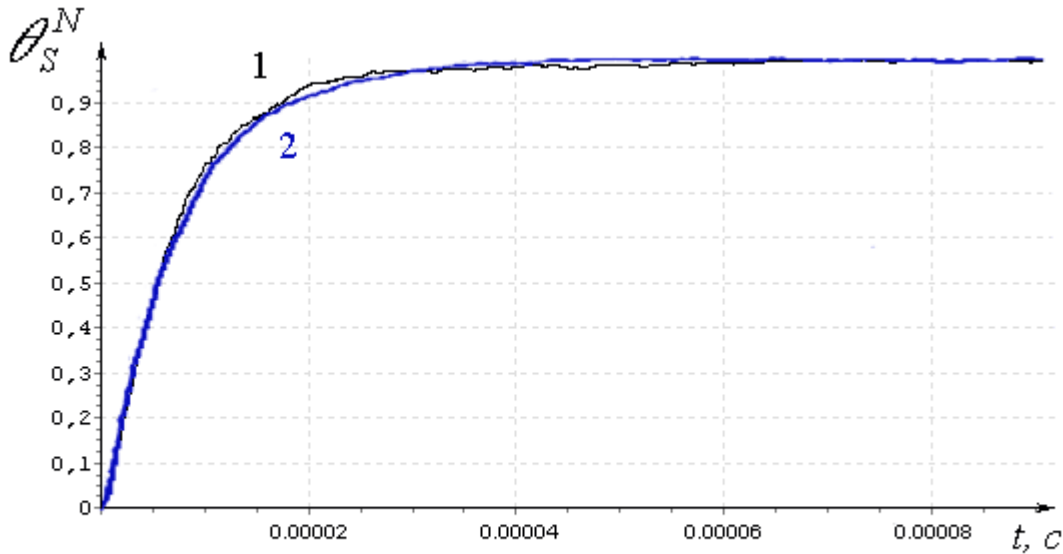


FIGURE 1. Comparison calculated physisorbed atom concentration (curve 2) with numerical results [5] (curve 1).

It is important, as one can see in Fig. 2, that calculated temperature dependence of nitrogen atom recombination probabilities on silicon based coating (continuous curve) agree well with experimental data [2] (squares).

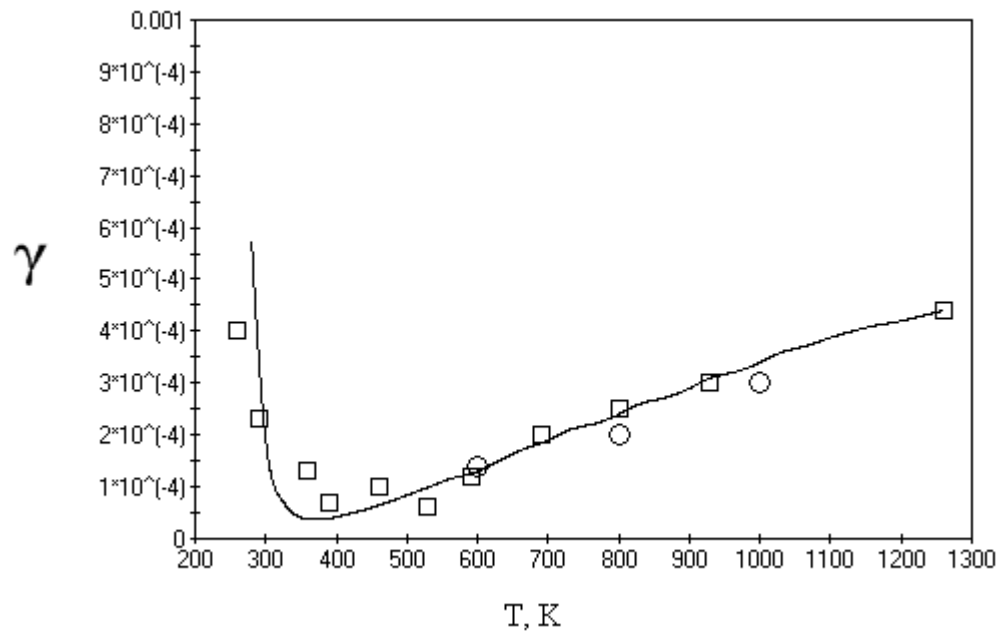


FIGURE 2. Temperature dependencies of nitrogen atom recombination probability. Squares are experimental results [4], continuous curve –calculations.

In Fig. 3 calculated dependences of physisorbed nitrogen atom stationary concentration and physisorbed oxygen atom stationary concentrations from gas atom concentration are presented.

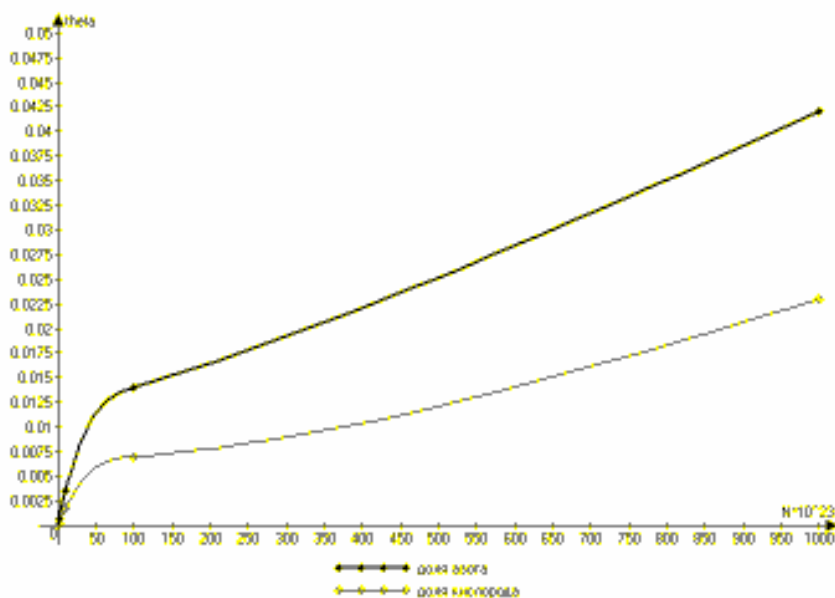


FIGURE 3. Gas atom concentration dependences of physisorbed nitrogen atom stationary concentration (bold curve) and physisorbed oxygen atom stationary concentrations

This figure shows that conditions in gas phase are very important for the heterogeneous catalytic recombination. The linear dependences of physisorbed atom stationary concentration at enough large values of gas atom concentration are found out.

CONCLUSION

Dynamic Monte Carlo method is developed for the simulation of the catalytic heterogeneous recombination in dissociated air. Shown that this method gives results, which agree well with known theoretical and experimental results. It is important, that it gives the same values of the recombination atom probability as in experiments. Thus, this method may be used to simulate the heterogeneous catalytic atom recombination on heat shield coatings of space vehicles. The advantage of a Monte Carlo simulation arises from the atomistic nature of this method, which easily provides physical insight into the basic phenomena occurring in the system.

ACKNOWLEDGMENTS

The authors thank the Russian Foundation for Basic Research (projects 05-01-00843 and Scientific .School-835.2006.1) for the financial support of this work.

REFERENCES

1. Kovalev V.L. Heterogeneous catalytic processes in an aerothermodynamics. M. Fizmatlit. 2002. 226 pp.
2. Kim Y.C., Boudart M. Recombination of O, N and H atom on silica: kinetics and mechanism // J. Langmuir. 1991. № 7. P. 2999-3005.
3. Fichthorn, K. A., and Weinberg, W. H., J. Chem. Phys., 95, 1090-1096 (1991).
4. Gordiets B.F., Ferreira C.M. Self-consistent modeling of volume and surface processes in air plasma // AIAA J. 1998. V. 36, № 9. P. 1643-1651.
5. V. Guerra and J. Loureiro, Dynamical Monte Carlo simulation of surface atomic recombination. Plasma Sources Sci. Techno. 13 (2004) 85-94.
6. Kovalev V.L., Kolesnikov A.F. Experimental and Theoretical Simulation of Heterogeneous Catalysis in Aerothermochemistry (a Review). Fluid Dynamics, vol. 40, No. 5, 2005.