# EFFECT OF SURFACE IMPURITIES ON ENERGY TRANSFER DURING ATOMIC ADSORPTION

V. V. Mazhuga

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The actual surface of a solid differs from the ideal surface because of the presence of various kinds of surface impurities and defects. It has been experimentally established [1] that the presence of foreign atoms on the surface of a crystal modifies the efficiency of energy transfer when a gas atom interacts with the surface. The problem of energy transfer between an atom and an actual solid is a very complicated one. Nonetheless, it is possible to explore the physics of the collision process by studying the behavior of simple mathematical models.

In Jackson's early theoretical study [2] the surface impurity is treated as an independent oscillator, which exchanges energy with the gas atom. However, when a gas atom collides with a surface, energy is transferred not only by the impurity atom, but also by the lattice atoms with which the surface impurity is linked. Thus, collision includes interaction with the normal vibrations of an imperfect crystal.

This problem was examined by McCarroll [3], who made computer calculations for the collision of an atom and a one-dimensional semi-infinite chain of atoms for several values of the mass for the impurity atom. He simulated surface impurity by varying the properties of the terminal atom of the chain. McCarroll confined himself to cases in which the mass of the impurity atom varies by only 20% as compared with the mass of the lattice atom, because his method of solving the equations of motion was not suitable for light impurity atoms. The presence of light impurity atoms on the surface, when local vibrations occur, is, however, a problem of great interest. When local vibrations occur, dissipation of the heat of adsorption is slowed greatly. The exact solution of this problem is obtained below.

A model of the collision of a gas atom with the surface of a crystal in the presence of an impurity is shown in Fig. 1; the atoms are numbered from right to left. The solid is approximated by a semi-infinite one-dimensional chain of atoms (mass M) coupled by elastic forces with the constant K. The terminal atom of the chain B (mass $M_1$) plays the part of impurity atom. We assume that the atom A (mass M) approaching from the gas phase can be adsorbed. The curve of the potential energy of interaction represents a cutoff harmonic oscillator with the force constant K.

The equation of motion for $x = r_0 - r_1$, where $r_0$ and $r_1$ are the deviations from the equilibrium position of the adsorbed and impurity atoms, respectively, has the form [3]:

$$4x^{\cdot\cdot}(\tau) + (\mu + 1)\,x(\tau) = 2\int_0^{\tau} \frac{J_2(s)}{s}\,[x(\tau - s) - 4(\mu - 1)\,x^{\cdot\cdot}(\tau - s)]\,ds\,, \tag{1}$$

$$\mu = M / M_1, \qquad \tau = 2(K/M)^{1/2}\,t = \omega_L t\,.$$

Here, $J_2(s)$ is a Bessel function of the second order.

The lattice is considered at 0° K, i.e., at the initial instant all the lattice atoms are at rest. Since in chemical adsorption the binding energy is much greater than the mean kinetic energy of the atoms in the gas phase, for simplicity it can be assumed that the velocity of the impinging atom is equal to 0. Accordingly, the initial conditions can be written in the form:

$$x(0) = a, \qquad x^{\cdot}(0) = 0\,, \tag{2}$$

where $a$ is the harmonic oscillator cutoff distance.

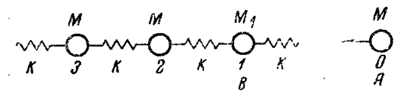

Fig. 1

We find the solution of Eq. (1) by the method described in [4].[*] By successive transformations the contour integral obtained is expressed in terms of Lommel, Bessel, and trigonometric functions. Before presenting the final results, to simplify the expressions we introduce the notation

$$C = \frac{(2 - 2\mu)\alpha^4 + (3 - 2\mu)\alpha^2 + 1 - \mu}{(1 - \mu)(\alpha^4 - \alpha^2\beta^2 - \alpha^2\gamma^2 + \beta^2\gamma^2)}\,, \tag{3}$$

$$D = \frac{(2 - 2\mu)\beta^4 + (3 - 2\mu)\beta^2 + 1 - \mu}{(\mu - 1)(\beta^4 - \alpha^2\beta^2 - \beta^2\gamma^2 + \alpha^2\gamma^2)}\,,$$

$$E = \frac{(2 - 2\mu)\gamma^4 + (3 - 2\mu)\gamma^2 + 1 - \mu}{(\mu - 1)(\gamma^4 - \alpha^2\gamma^2 - \beta^2\gamma^2 + \alpha^2\beta^2)}\,,$$

$$\alpha = [{}^2/_3 \sqrt{2}\,\theta(\mu)\,\mathrm{sh}\,{}^1/_3\varphi - {}^2/_3]^{1/2}\,,$$

$$\beta = [-{}^1/_3 \sqrt{2}\,\theta(\mu)\,\mathrm{sh}\,{}^1/_3\varphi - {}^2/_3 - {}^1/_3\,i\sqrt{6}\,\theta(\mu)\,\mathrm{ch}\,{}^1/_3\varphi]^{1/2}\,,$$

$$\gamma = [-{}^1/_3 \sqrt{2}\,\theta(\mu)\,\mathrm{sh}\,{}^1/_3\varphi - {}^2/_3 + {}^1/_3\,i\sqrt{6}\,\theta(\mu)\,\mathrm{ch}\,{}^1/_3\varphi]^{1/2}\,,$$

$$\theta(\mu) = \begin{cases} 1, & \mu > 1, \\ -1, & \mu < 1, \end{cases} \qquad \mathrm{sh}\,\varphi = \frac{20\mu + 7}{4\sqrt{2}\,|\mu - 1|}\,.$$

Then the solution can be written in the form:

when $\mu \leqslant {}^6/_5$ and $\mu \neq 1$,

$$x(\tau) = x(0)\,[J_0(\tau) - C\,U_2(\alpha^{-1}\tau,\tau) + D\,U_2(\beta^{-1}\tau,\tau) + E\,U_2(\gamma^{-1}\tau,\tau)]\,, \tag{4}$$

when $\mu > {}^6/_5$,

$$x(\tau) = x(0)\,[J_0(\tau) + C\cos\,\omega\tau - C\,U_0(\alpha\tau,\tau) + D\,U_2(\beta^{-1}\tau,\tau) + E\,U_2(\gamma^{-1}\tau,\tau)]\,,$$

$$\omega = {}^1/_2(\alpha^2 + 1)/\alpha\,. \tag{5}$$

Here, $U_2(\alpha^{-1}\tau, \tau)$ is a Lommel function of two variables; the solution was previously obtained in [5] for $\mu = 1$.

This solution makes it possible to study the effect of surface impurities on the establishment of thermal equilibrium when an atom is adsorbed. Since a fairly considerable amount of energy is usually released in chemical adsorption, the atom is initially in a highly energetic state and must approach equilibrium with the solid in an oscillatory process at the surface. It is easy to show that in the formulas for $x(\tau)$ all the terms vanish as $\tau \to \infty$, except for the term containing the cosine. The latter corresponds to excitation of local vibration whose energy is not dissipated into the lattice in the harmonic approximation, but remains with the given atom.

The frequency of local vibration of the impurity atom, expressed in relative units $\omega = \omega_0/\omega_L$ ($\omega_0$ is the frequency of the local vibration), is shown in Fig. 2 as a function of the mass ratio $\mu = M/M_1$. In the presence of light impurity atoms on the surface of a solid the local vibration frequency exceeds the Debye frequency $\omega_L$ by several times.

The relative amplitude of the local vibration C is shown in Fig. 3 as a function of the mass ratio. It is clear from Fig. 3 that as the mass of the impurity atom decreases the amplitude of the local vibration rapidly increases from 0 to 0.5. In the presence of light surface impurities about half the energy released in connection with adsorption can remain at the surface in the form of a local vibration of the impurity atom.

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[*] In [4] a mistake was made in writing out the Bessel functions. The quantity $I_\nu(\tau)$ should be replaced everywhere by $J_\nu(\tau)$, i.e., by Bessel functions of a real argument.

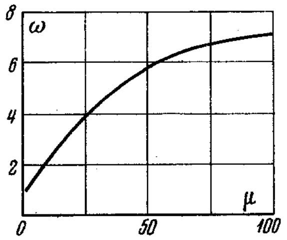

Fig. 2

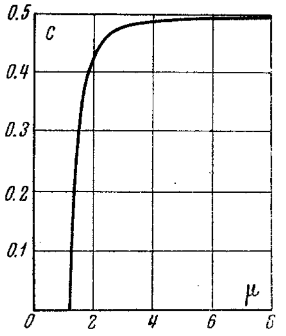

Fig. 3

From this it is clear that in the course of a chemical reaction light impurity atoms at the catalyst surface can absorb a certain part of the energy released during adsorption and the exothermic elementary events of the process. This energy is concentrated in the vibrational degrees of freedom of the impurity atoms. As a result relatively long-lived, vibrationally excited particles appear at the catalyst surface, their concentration being above the equilibrium value. Subsequently, the excess energy of the vibrationally excited particles can be transferred to the substrate molecules, thus lowering the activation energy.

The phenomenon of activation of thin layers of metal with microquantities of gases—nitrogen, hydrogen, oxygen—has long been known [6]. The mechanism of activation with small doses of gases can be explained in terms of the formation of an impurity in the catalyst lattice and of an increase in the impurity supersaturation, as a result of which new active centers capable of absorbing a certain part of the energy released in the elementary reaction events are created.

## REFERENCES

1. H. Wachman, "The role of the surface in thermal accommodation," Symp. on Dynamics of Manned-Lifting Planetary Entry, Wiley, New York—London, p. 778, 1963.

2. J. Jackson, "A quantum mechanical theory of energy exchange between inert gas atoms and a solid surface," Proc. Cambridge Philos. Soc., vol. 28, p. 136, 1932.

3. B. McCarroll, "Trapping and energy transfer in atomic collisions with a crystal surface, II, Impurities," J. Chem. Phys., vol. 39, no. 5, p. 1317, 1963.

4. V. V. Mazhuga, "Collision of an atom with the surface of a solid," PMTF [Journal of Applied Mechanics and Technical Physics], no. 3, p. 126, 1966.

5. N. Cabrera, "Structure of crystal surfaces," Disc. Faraday Soc., no. 28, p. 16, 1959.

6. S. Z. Roginskii, Adsorption and Catalysis on Inhomogeneous Surfaces [in Russian], Izd-vo AN SSSR, 1948.

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