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Three-levels model kinetics for atom recombination at catalytic surfaces

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Abstract

A model kinetics is presented for describing adatom recombination ruled by the 'hot atom' mechanism. Hot atoms are identified with adatoms populating the excited vibrational states of the adsorption potential well. The disposal of vibrational quanta to the solid and the transfer of quanta among adatoms are taken into account by the kinetics. In the model case of three-levels the kinetics is solved analytically. It is shown that the competition between recombination and quantum transfer to the solid may drive the system far from equilibrium, leading to an enhancement of the reaction rate. The equilibrium non-equilibrium transition is studied in terms of control parameters, such as the gas flux and the vibrational relaxation time, and it is further characterized through the behaviour of the ''apparent'' activation energy of the reaction which is found to depend, strongly, on the vibrational state of the adlayer.

Keywords: Kinetics; Adatom recombination; Non equilibrium phenomena

1. Introduction

In exoergic processes at catalytic surfaces, such as atom recombination, the energy released during the reaction can be used to excite either the desorbing molecules or the adsorbed species. In general, a large fraction of the reaction energy is available to the adlayer–substrate system and, in this respect, one wonders about the possibility that a part of this energy be used to rule more facile reaction routes, the remaining part being dissipated into the substrate [1–3]. As a matter of fact the rate of the process is affected by the reaction pathway and can lead to a reaction mechanism that is intermediate between the Langmuir–Hinshelwood (LH) and the Eley–Rideal (ER), namely the ''hot atom'' precursor mechanism (HA) [4–6].

On the theoretical side the modelling of the HA mechanism requires the determination of the HA surface coverage which, in the model case of flat surfaces, can be identified, quite naturally, with the populations of adatoms in the vibrational states of the potential well. This approach has firstly been applied to chemisorption [7] where the vibrational populations have been computed by a kinetic approach under quasi-steady state conditions. In a successive work we dealt with the recombination process by means of numerical integration of rate equations for a four-levels system [8]. It is worth noticing that these modelling apply to reactions under steady state (or quasi-steady state) conditions, where the surface density of HA takes a constant value. Specifically, by denoting with τ the HA life-time and with Φ the steady state recombination rate (i.e. the adsorption rate), the surface coverage of HA, σ_{HA}, is of the order of magnitude of $\sigma_{HA} \approx \Phi\tau$. In spite of the short life-time of the ''transient'' species, σ_{HA} can be much larger than the corresponding Boltzmann populations, leading to hyperthermal reaction rates. In fact, diatom formation arises by reaction channels involving pairs of HA in different vibrational levels, provided the total energy is greater than the activation barrier.

Recently, the steady state vibrational distributions of the adatoms during recombination have been computed, analytically, in the case of single- and multi-quantum transfer to the solid [9,10]. It is shown that to ensure the conservation of vibrational quanta (as it is required at steady state) the vibrational distributions are, in general, hyperthermal. The effect of the displacement from equilibrium on the recombination rate was also investigated in Refs. [9,10]. It was shown that a transition towards non-equilibrium vibrational states can

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occur which is accompanied by an enhancement of the recombination rate. In Ref. [11] the process of energy transfer from the adsorbing atoms to the adlayer has been tackled by solving the Fokker–Planck equation in energy space. By resorting to approximation the equation is solved in closed form for the steady state energy distribution of the adspecies. Also, in this modelling the transition from the LH to the HA-precursor mechanism has been studied in terms of catalyst parameters.

The aforementioned analytical approaches were mainly concerned to model steady state conditions, i.e. they were not employed for describing the whole kinetics of the adsorption–recombination process. The purpose of the present contribution is to model the entire kinetics of the reaction by solving, in closed form, rate equations in the case of few vibrational levels.

2. Results and discussions

In the following we present rate equations for a three-levels system. Reduction of the complexity of the vibrational ladder to three-levels allows for an analytical solution of the system, which gives the time evolution of the recombination rate, of the total surface coverage and of the energy distribution of adatoms. Therefore, thanks to the analytical solution it is also possible to study the reaction rate and the coverage behaviour in the transient regime, that is before the attainment of the steady state.

We consider the three-levels labelled as 0, p and ν^* namely the ground level (0), the upper bound level (ν^*) and an intermediate state (p) at $E_p < E_{\nu^*}$, where E_n is the adatom vibrational energy as measured from the bottom of the adsorption potential well. Recombination is assumed to arise by binary encounter of adatoms in states 0 and p under quasi steady state condition of the vibrational ladder [9,10]. By denoting with σ_ν the population of the νth level, the rate equations read

$$\frac{d\sigma}{dt} = J(\sigma) - \Phi \tag{1}$$

$$I_{p,0} = J(\sigma) - \frac{\Phi}{2} \tag{2}$$

$$\Phi = 2Z\sigma_0\sigma_p \tag{3}$$

where Φ is the recombination rate expressed in atoms per unit time, Z the rate constant for dimer formation, σ the total surface coverage, $J(\sigma)$ the net flux of gas-atoms entering the potential well from the upper bound level and $I_{p,0}$ is the current of adatoms from level p to level 0 due to the exchange of vibrational quanta with the solid (VL scattering) and with the adatoms (VV scattering). This last term has been computed in [7,9] in terms of the coverage dependent rate coefficients for VL and VV quantum exchange:

$$I_{p,0} = \sigma_p(K_{VL} + P^{(r)}) - \sigma_0(K_{VL}\, e^{-\beta\Delta E_{p,0}} + P^{(f)}) \tag{4}$$

where $\Delta E_{p,0} = E_p - E_0$ and $\beta = (k_B T)^{-1}$, k_B being the Boltzmann constant and T the temperature of the surface. In Eq. (4) K_{VL} and P denotes the first order rate coefficients for the VL and VV scatterings, respectively, where the superscripts (r) and (f) denote the direct and the reverse process, respectively. Also, the detailed balance has been used to link the forward (K_{VL}) and the backward rate constants of the VL exchange. The P rate coefficients are given by,

$$P^{(r)} = P_{p,0\to 0,p}\sigma_0 + P_{p,p\to 0,\nu^*}\sigma_p \tag{5a}$$

$$P^{(f)} = P_{0,p\to p,0}\sigma_p + P_{0,\nu^*\to p,p}\sigma_{\nu^*} \tag{5b}$$

where $P_{i,j\to k,l}$ is the rate constant for the quantum transfer among adatoms according to [10]:

$$A(i) + A(j) \overset{P_{i,j\to k,l}}{\longrightarrow} A(k) + A(l).$$

We employ Eqs. (5a) and (5b) under the reasonable assumption $\sigma \cong \sigma_0$ and for rate constants independent of quantum numbers: $P_{i,j\to k,l} = P_{VV}$. From Eqs. (5a) and (5b) we get $\sigma P^{(f)} - \sigma_p P^{(r)} = P_{VV}[\sigma\sigma_{\nu^*} - \sigma_p^2]$ and the Eq. (4) reduces to

$$I_{p,0} = K_{VL}\left(\frac{\Phi}{2Z\sigma} - \sigma\, e^{-\beta\Delta E_{p,0}}\right) - P_{VV}(\sigma\sigma_{\nu^*} - \sigma_p^2) \tag{6}$$

where use was made of Eq. (3) to eliminate the σ_p dependence in favour of the recombination flux. From Eqs. (1)–(6) one obtains the relationship

$$\frac{K_{VL}}{2Z\sigma} = \frac{\dot\sigma + \Phi/2 + P_{VV}(\sigma\sigma_{\nu^*} - \sigma_p^2)}{\Phi - 2Z\sigma^2\, e^{-\beta\Delta E_{p,0}}} \tag{7}$$

that can be further simplified by exploiting the expression of the $I_{\nu^*,p}$ current:

$$I_{\nu^*,p} = \sigma_{\nu^*}(K_{VL} + P'^{(r)}) - \sigma_p(K_{VL}\, e^{-\beta\Delta E_{\nu^*,p}} + P'^{(f)}) \tag{8}$$

with

$$P'^{(r)} = P_{VV}\sigma_0 + P_{VV}\sigma_p \tag{8a}$$

$$P'^{(f)} = P_{VV}\sigma_p + P_{VV}\sigma_{\nu^*} \tag{8b}$$

By using the quasi-steady state condition $J(\sigma) = I_{\nu^*,p}$ together with Eqs. (8a) and (8b), the Eq. (8) can be recast in the form

$$J(\sigma) = \sigma_{\nu^*}K_{VL} - \frac{\Phi}{2Z\sigma}K_{VL}\, e^{-\beta\Delta E_{\nu^*,p}} + P_{VV}(\sigma\sigma_{\nu^*} - \sigma_p^2) \tag{9}$$

from which the $P_{VV}(\sigma\sigma_{\nu^*} - \sigma_p^2)$ term can be elaborated. Accordingly, Eq. (7) becomes

$$\frac{K_{VL}}{2Z\sigma} = \frac{2\dot\sigma + (3/2)\Phi}{\Phi(1 - e^{-\beta\Delta E_{\nu^*,p}}) - 2Z\sigma(\sigma\, e^{-\beta\Delta E_{p,0}} - \sigma_{\nu^*})} \tag{10}$$

where Eq. (1) was employed. The vibrational population of the upper bound level, ν^*, is obtained from Eq. (9) according to

$$\sigma_{\nu^*} = \frac{1}{1+\chi\sigma}\left[\frac{J(\sigma)}{K_{VL}} + \sigma_p(e^{-\beta\Delta E_{\nu^*,p}} + \chi\sigma_p)\right] \tag{11}$$

where $\chi = P_{VV}/K_{VL}$. From the expression Eq. (10) one also evaluates the adsorption rate as a function of surface coverage.

For $e^{-\beta \Delta E_{v^*,p}} \ll 1$ the kinetics reads

$$\frac{d\sigma}{dt} = \frac{1}{(\sigma + 2\rho)} [J(\sigma)(2\rho - 3\sigma) - 4Z\rho\sigma(\sigma e^{-\beta \Delta E_{p,0}} - \sigma_{v^*})] \quad (12)$$

with $\rho = K_{VL}/2Z$.

Let us draw our attention to the direct random adsorption where $J(\sigma) = J(1 - \sigma)$, J being the flux of gas atoms impinging on the surface. In the following we deal with the case $\chi \ll 1$, i.e. when the VL scattering is the main channel for the transfer of vibrational quanta. In addition, since the term in the last brackets of Eq. (11) can be neglected when compared to the first one (see below), the population of the upper bound level is given by $\sigma_{v^*} \cong J(1 - \sigma)/K_{VL}$. In the case of recombination of light atoms, such as H or D, we consider $K_{VL} < 10^{13}\ s^{-1}$ and $e^{-\beta \Delta E_{v^*,p}} \cong e^{-\beta \Delta E_{p,0}} < 10^{-15}$ [12]. Moreover, we limit our analysis to the case $J > 10^{-2}\ s^{-1}$. Consequently, being $J/K_{VL} > 10^{-15}$, the aforementioned approximate expression of σ_{v^*} is expected to hold. Under these circumstances Eq. (12) eventually reduces to

$$\frac{d\sigma}{dt} = \frac{1}{(\sigma + 2\rho)} [J(1 - \sigma)(2\rho - \sigma) - 4Z\rho\sigma^2 e^{-\beta \Delta E_{p,0}}] \quad (13)$$

with solution

$$Jt = \left(2\rho - \frac{b}{2c}\right) \frac{1}{\Delta^{1/2}} \ln \left[\frac{(2c\sigma + b - \Delta^{1/2})(b + \Delta^{1/2})}{(2c\sigma + b + \Delta^{1/2})(b - \Delta^{1/2})} \right] + \frac{1}{2c} \ln \frac{a + b\sigma + c\sigma^2}{a} \quad (14)$$

where $a = 2\rho$, $b = -(1 + 2\rho)$, $c = 1 - 4(Z/J)\rho e^{-\beta \Delta E_{p,0}}$, $\Delta = b^2 - 4ac$ and the initial condition $\sigma(0) = 0$. From the $\sigma(t)$ kinetics the recombination rate is estimated from Eq. (1). Furthermore, at steady state (s) Eq. (13) gives $K_{VL}/Z\sigma_s = \Phi_s/(\Phi_s - 2Z\sigma_s^2 e^{-\beta \Delta E_{p,0}})$, which indicates that in the limit $\Phi_s \gg 2Z\sigma_s^2 e^{-\beta \Delta E_{p,0}}$ the surface coverage depends upon the K_{VL}/Z ratio only: $\sigma_s = K_{VL}/Z$.

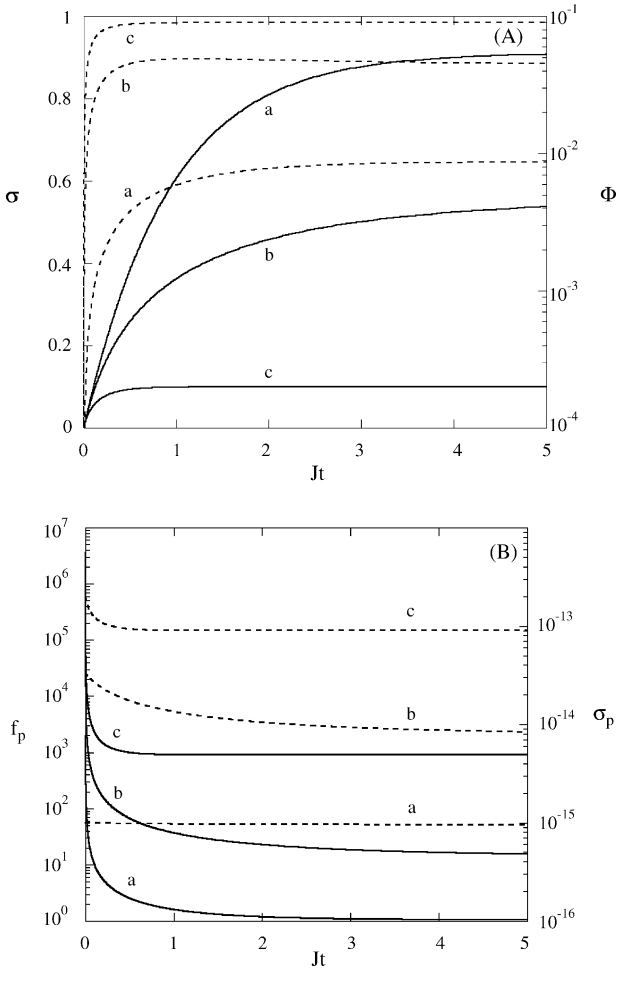

Fig. 1. Kinetics of adsorption and recombination as a function of the exposure (Jt). In panel A, the surface coverage, σ, and the recombination rate, Φ, are shown as full and dashed lines, respectively. In panel B, the behaviour of both f_p and σ_p are displayed as full and dashed lines, respectively. Parameter values are: $e^{-\beta \Delta E_{p,0}} = 10^{-15}$, $J = 0.1\ s^{-1}$, $\rho = 10$ (curve a), $\rho = 0.3$ (curve b), $\rho = 0.05$ (curve c) where $\rho = K_{VL}/2Z$.

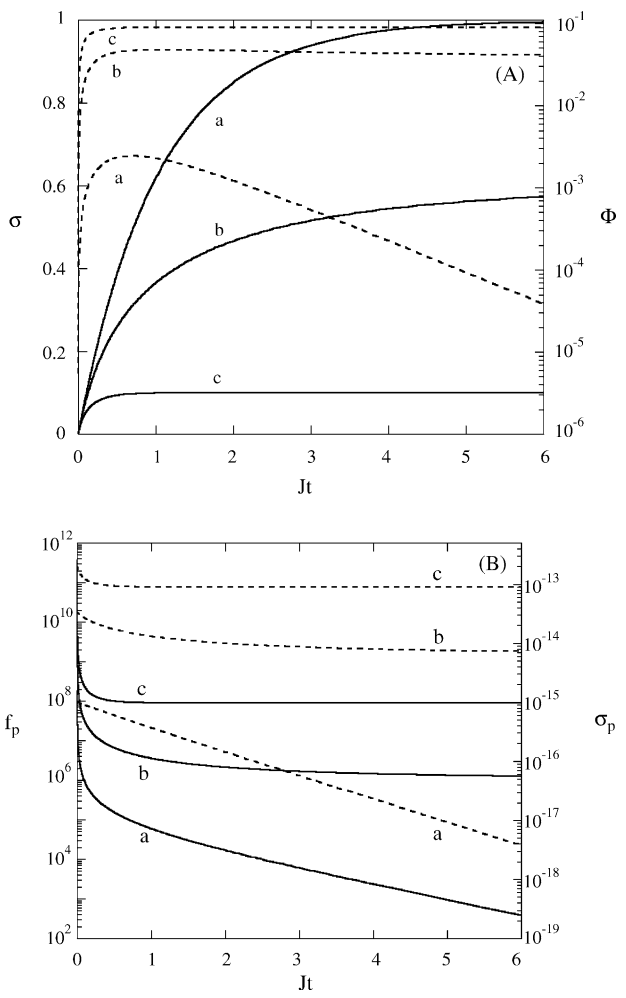

Fig. 2. Kinetics of adsorption and recombination. Panel A: surface coverage (full lines) and recombination rate (dashed lines). In panel B, the behaviour of both f_p and σ_p are displayed as full and dashed lines, respectively. Parameter values are: $e^{-\beta \Delta E_{p,0}} = 10^{-20}$, $J = 0.1\ s^{-1}$, $\rho = 10$ (curve a), $\rho = 0.3$ (curve b), $\rho = 0.05$ (curve c).

An interesting result of this model stems from the analysis of the steady state by means of Eq. (13). It is worth to remind that the steady state condition is reached at the end of the adsorption process. By setting $\dot{\sigma} = 0$ in Eq. (13) it is possible to compute the steady state value of the surface coverage as a function of ρ and Z and, consequently, to evaluate the recombination rate $\Phi_s/J = 1 - \sigma_s$. The expression reads,

$$\frac{\Phi_s}{J} = 1 - \frac{-(1/2+\rho) + \sqrt{(\rho - 1/2)^2 + 4\rho^2(2Z/J)\,e^{-\beta\Delta E_{p,0}}}}{(4Z\rho\,e^{-\beta\Delta E_{p,0}}/J) - 1} \tag{15}$$

Typical behaviour of the adsorption–recombination kinetics Eq. (14), are displayed in Figs. 1 and 2 for several values of the catalyst parameters, namely ρ, J and $\beta\Delta E_{p,0}$. The total surface coverage and the recombination rate are shown in panels A while the populations of the level p are shown in panels B. As a possible measure of the overpopulation of the p-level we define the quantity $f_p = (\sigma_p/\sigma_0)/(\sigma_p/\sigma_0)_B = (\sigma_p/\sigma_0)\,e^{\beta\Delta E_{p,0}}$ where the subscript B indicates the Boltzmann distribution. The kinetics of the overpopulation factor is also shown in panels B. The adsorption kinetics are found to be very well described by the first order kinetics $\dot{\sigma} = J\alpha(\sigma(\infty) - \sigma)$ where α is a constant. In spite of the fact that the characteristic times for VL and VV processes are of the order of magnitude of 10^{-13} s, Figs. 1 and 2 show that the characteristic time for the reaching of the steady state is of the order of magnitude of J^{-1} ($\approx$10 s). This is the expected result which is also in agreement with the experimental findings. It therefore stems that the kinetic model correctly deals with the different time scales of the considered processes.

As it appears from Figs. 1 and 2 the recombination rate at steady state are strongly dependent on the ρ parameter. In particular, this dependence is given by Eq. (15) whose behaviour, as a function of the $\rho = K_{VL}/2Z$ ratio, is displayed in Fig. 3. This result indicates that the reaction rate increases as ρ decreases and the reaction rate, for the Boltzmannian distribution, is practically recovered at $\rho > 1$. On the other side the kinetics displayed in Figs. 1 and 2 (panels B) show that such a behaviour of the reaction rate is ascribed to a continuous transition of the vibrational state of the adlayer, which is accompanied by an increase of the overpopulation factor. Let us

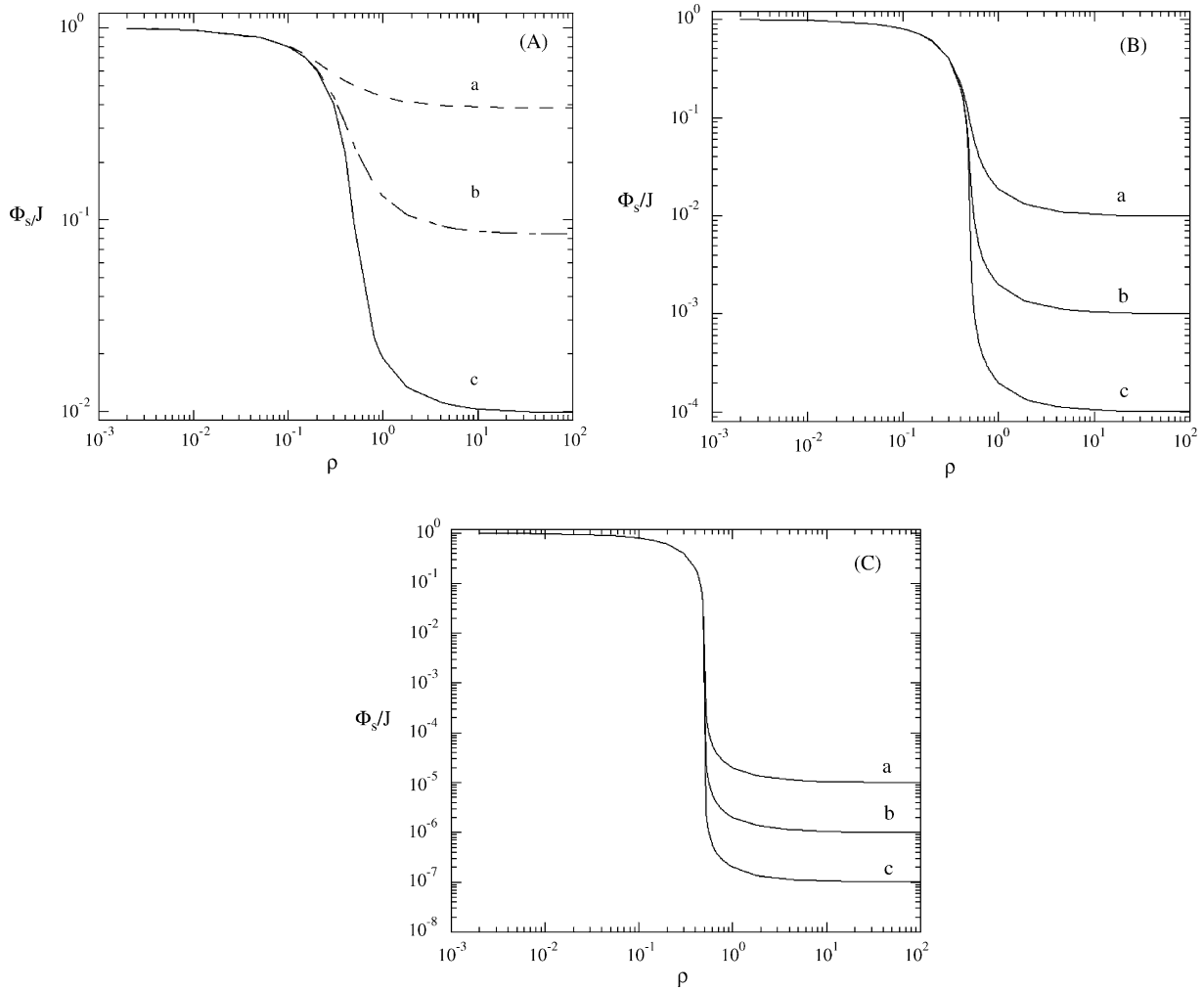

Fig. 3. Steady state values of the recombination rate as a function of ρ, for $J = 0.01\ s^{-1}$ (curve a), $J = 0.1\ s^{-1}$ (curve b) and $J = 1\ s^{-1}$ (curve c). Panels A, B and C refer, respectively, to the cases $e^{-\beta\Delta E_{p,0}} = 10^{-15}, 10^{-17}, 10^{-20}$.

consider in more detail this transition. We observe that Eq. (15) is equivalent to the general solution attained in Ref. [10] for the recombination channel 0–p and in the limit $\chi \ll 1$. Moreover, the solution reported in Ref. [10] holds in the harmonic case and for single quantum transfer. From Fig. 3 one also appreciates that these curves are quite steep in the proximity of $\rho \cong 1/2$; the kinetic transition occurs for $K_{VL} \cong Z$ that is when the probability for atom recombination is close to the probability for quantum exchange to the solid. As a matter of fact for $2(Z/J)\,e^{-\beta\Delta E_{p,0}} \ll 1$ the Φ_s/J function is characterized by two distinct regimes that can be studied through the series expansion of Eq. (15) in the $\zeta \equiv 2(Z/J)\,e^{-\beta\Delta E_{p,0}}$ variable. The computation leads to

$$\left.\frac{\Phi_s}{J}\right|_{\rho>1/2} = \left(\frac{2\rho}{2\rho-1}\right)\zeta \tag{16}$$

and

$$\left.\frac{\Phi_s}{J}\right|_{\rho<1/2} = 1-2\rho \tag{17}$$

where ζ is equal to the recombination rate (normalized to the J flux) in the case of a Boltzmann distribution of the vibrational levels that is attained in the limit $\rho \to \infty$. Furthermore, in the second regime the recombination rate can exceed the Boltzmann rate by several order of magnitude depending on the $\Delta E_{p,0}$ value. To be specific, on logarithmic scale such an enhancement is approximately given by $(\log e)\beta\Delta E_{p,0}$. On the contrary, for $\zeta > 1$, as it occurs for small values of the depth of the potential well, the transition becomes smooth. The ratio between the recombination rates above and below the transition point are of the order of magnitude of $(1-\zeta^{-1/2})^{-1}$; on logarithmic scale this implies a jump of about $\zeta^{-1/2} \ll 1$.

The transition discussed so far has important consequences on the behaviour of physical quantities, usually employed for characterizing the catalyst activity, such as the ''apparent'' activation energy of the reaction: $E^{\#}$. Since we are dealing with second order reaction, the activation energy can be estimated, at steady state, through the Arrhenius plot of the $\Phi_s/2Z\sigma_s^2$ quantity. In fact, for the Boltzmann distribution the steady state reaction rate is $\Phi_s = 2Z(\sigma_0\sigma_p)_s = 2Z\sigma_s^2\,e^{-\beta\Delta E_{p,0}}$. The results are shown in Fig. 4 for two values of the activation energy, $\Delta E_{p,0}$, and for several values of ρ. The Arrhenius plot are computed for $J = 0.1$, $Z = 5 \times 10^{12}\ s^{-1}$ and in the temperature interval 50–200 K. As it appears, the impact of the non-equilibrium state of the adlayer on $E^{\#}$ can be dramatic depending upon K_{VL}/Z. In particular, at a given $\Delta E_{p,0}$ value the apparent activation energy is a decreasing function of Z/K_{VL} which vanishes once the kinetic transition takes place. Moreover, for $\rho < 1/2$ the effect of the transition on $E^{\#}$ becomes negligible as the temperature rises and all curves yield the $\Delta E_{p,0}$ activation energy. This is expected to occur at temperatures for which the inequality $4\rho^2\zeta > 1$ is fulfilled; these temperatures being dependent on the activation energy. In other words, on the ground of the aforementioned associative model, it stems that the shape of the energy distribution of adatoms determines the reaction rate and, under non-equilibrium condition, reactions with different ''true activation energies'' can proceed at comparable rate at finite surface temperature. This argument gives a possible explanation to the so called ''compensation effect'' in catalysis, also known as ''Θ'' rule, as discussed in [13].

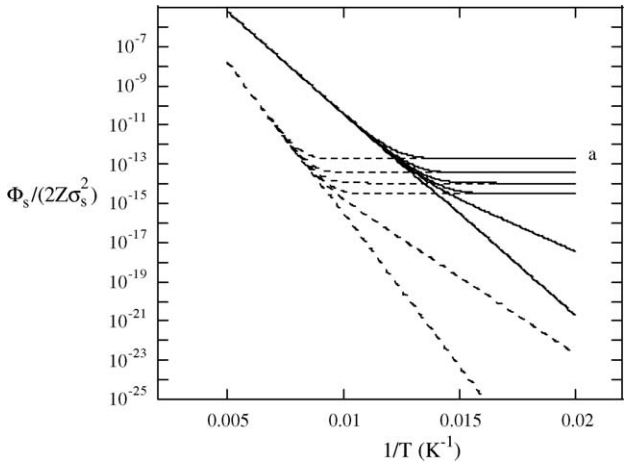

Fig. 4. Arrhenius plot of $\Phi_s/2Z\sigma_s^2$ as a function of ρ, for $J = 0.1\ s^{-1}$, $\Delta E_{p,0} = 20$ kJ/mol (full lines) and $\Delta E_{p,0} = 30$ kJ/mol (dashed lines). From the top (curves a): $\rho = 0.1$, 0.2, 0.3, 0.4, 0.5 and 1.5.

Before concluding a comment on Eq. (13) is in order. Although it has been formulated for $J(\sigma) = J(1-\sigma)$, it can also be employed for different form of the $J(\sigma)$ function. Work is in progress aimed at describing experimental data through Eq. (12) by making use of the experimental $J(\sigma)$.

3. Conclusions

In spite of its simplicity, the kinetics discussed so far has the merit to throw light on the effect of the energy disposal to the solid on the reaction rate. As a matter of fact the reaction rate under equilibrium condition, namely for a Boltzmann distribution of the vibrational ladder, is independent of K_{VL} and P_{VV} as it is easily attained in the limit $K_{VL} \to \infty$.

The analytical approach gives the behaviour of the recombination rate and of the surface coverage in the transient regime. The steady state recombination rate is studied as a function of both activation energy, $\Delta E_{p,0}$, and K_{VL}/Z ratio. It is shown that for direct random adsorption the reaction rate is an increasing function of Z/K_{VL} and such a behaviour is linked to a transition of the vibrational state of the adlayer. This transition is also accompanied by a reduction of the ''apparent'' activation energy for recombination. Although the computation refers to few levels, these conclusions are quite general and can be extended to multi-level systems as well [10,13].

References

[1] L. Romm, M. Asscher, Y. Zeiri, J. Chem. Phys. 110 (1999) 11023.
[2] Z. Knor, Appl. Catal. A 245 (2003) 185.
[3] B. Gumhalter, T. Matsushima, Surf. Sci. 561 (2004) 183.
[4] S. Wehner, J. Küppers, J. Chem. Phys. 108 (1998) 3353.
[5] A.F. Carley, P.R. Davies, M.W. Roberts, Catal. Lett. 80 (2002) 25.
[6] R. Burch, S.T. Daniells, J.P. Breen, P. Hu, Catal. Lett. 94 (2004) 103.

[7] M. Tomellini, Surf. Sci. 544 (2003) 209;
E. Molinari, M. Tomellini, Surf. Sci. 552 (2004) 180.
[8] M. Tomellini, Surf. Sci. 556 (2/3) (2004) 184.
[9] M. Tomellini, Surf. Sci. 577 (2005) 200.
[10] E. Molinari, M. Tomellini, Catal. Today, this issue.
[11] V.P. Zhdanov, Surf. Sci. 575 (2005) 313.
[12] E. Molinari, M. Tomellini, Chem. Phys. 270 (2001) 439.
[13] E. Molinari, M. Tomellini, Catal. Lett. 83 (2002) 71.