Catalysis Letters Vol. 83, No. 1–2, October 2002 (©2002)

Vibrational non-equilibrium at catalytic surfaces

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Received 26 March 2002; accepted 31 May 2002

Inclusion in a surface reaction scheme of fast V-V up-pumping processes, bound to the anharmonicity of the vibrational levels of mobile surface species, can lead to quasi-steady states characterized by non-equilibrium Treanor vibrational distribution functions, with $\nu > 0$ levels over-populated with respect to Boltzmann equilibrium. Non-equilibrium distributions are shown to depend on the intensity of the chemisorption processes active under the working conditions of the catalyst. The shape of these distributions determines the surface reaction rate, and reactions with widely different "true" activation energies can proceed at comparable speeds at finite surface temperatures. This provides an interpretation of the isokinetic relationship in heterogeneous catalysis based on a non-Boltzmann picture of the catalytic surface.

KEY WORDS: adlayers; heterogeneous catalysis; isokinetic relationship; non-equilibrium (vibrational); surface vibrations; surface kinetics.

1. Introduction

An alternative statistical description of the state of a catalytic surface under working conditions is presently emerging from a series of papers showing that the current, tacit assumption that the vibrational distribution functions (vdf) of chemisorbed species correspond to Boltzmann equilibrium actually leads to conclusions incompatible with experimental observations [1–4]. The suggestion was therefore made [1,2] that, in the quasi-steady-state of a working catalytic surface, vdfs should rather be described by non-equilibrium equations, such as the Treanor or similar ones [5,6], exhibiting an over-population of the $\nu > 0$ vibrational levels with respect to the corresponding Boltzmann equilibrium distributions at the surface temperature T_s. Issues of this work will be examined with the aim of providing a non-equilibrium description of a working catalytic surface with some of the basic consequences connected with non-equilibrium quasi-steady-states.

2. Non-equilibrium vibrational kinetics in the adlayer

Let us select, as an example, the catalytic oxidation of CO by either molecular, $O_{2(g)}$, or atomic, $O_{(g)}$, gaseous oxygen on noble metal catalysts [4].

It is a well-established fact that the surface reaction $CO_{(s)} + O_{(s)} \Rightarrow CO_{2(g)}$ is the rate-determining step of the heterogeneous oxidation of carbon monoxide on metallic surfaces (subscript (s) denotes a chemisorbed species). Figure 1 gives a potential energy profile for this reaction [7–9] (Langmuir–Hinshelwood (LH) mechanism). Figure 2 gives qualitative profiles for chemisorbed oxygen (a) and chemisorbed CO (b) with the corresponding anharmonic vibrational levels $\nu = i$ and $\nu = j$ respectively. The initial step of $O_{(g)}$ chemisorption corresponds to a *pump* process *populating* the upper i^* level of the S–O species,

$$O_{(g)} \Rightarrow O_{(s)}\,(i = i^*) \tag{1a}$$

while chemisorption of $O_{2(g)}$ pumps a lower i^+ level (figure 2(a))

$$O_{2(g)} \Rightarrow 2O_{(s)}\,(i = i^+). \tag{1b}$$

Chemisorption of $CO_{(g)}$ populates the upper j^* level of the vibrational ladder of the S–CO species,

$$CO_{(g)} \Rightarrow CO_{(s)}\,(j = j^*) \tag{1c}$$

(figure 2(b)). The vibrational energy pumped into these excited vibrational levels by the chemisorption processes is redistributed over the entire vibrational manifolds of the adspecies by V-V and by V-L processes.

For a non-resonant V-V exchange among *mobile* surface *anharmonic* oscillators $O_{(s)}$ or $CO_{(s)}$, with energies given by

$$E(\nu) = \nu E_{10}[1 - \delta(\nu - 1)] \tag{2}$$

as measured from level $\nu = 0$ using a simple model of the anharmonic Morse oscillator ($\delta = \Delta E/E_{10}$, with ΔE the anharmonicity of the oscillator and E_{10} the energy spacing between levels $\nu = 0$ and $\nu = 1$) one writes

$$O_{(s)}(\nu = 1) + O_{(s)}(\nu) \underset{P_r}{\overset{P_f}{\rightleftharpoons}} O_{(s)}(\nu = 0) + O_{(s)}(\nu + 1) \tag{3}$$

and similarly for $CO_{(s)}$.

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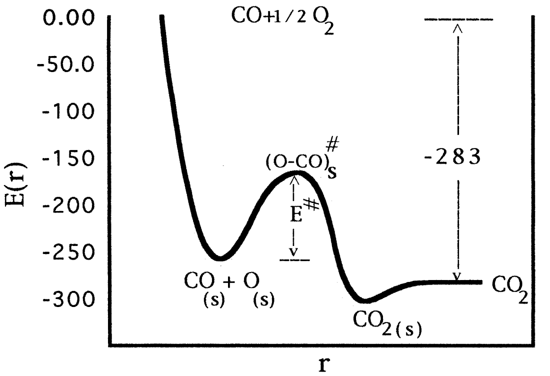

Figure 1. Energy diagram for the reaction $CO_{(s)} + O_{(s)} \Rightarrow CO_{2(g)}$.

Application of detailed balancing to reaction (3) yields

$$P_f = P_r \exp\left(\frac{2E_{10}\delta\nu}{RT_s}\right). \tag{4}$$

This means that forward pumping, P_f, *i.e.*, up-pumping, is faster than reverse pumping, P_r, with the net result of *over*-populating the vibrational levels with respect to a Boltzmann distribution. Equation (4) reflects the anharmonicity of vibrational levels. In fact, the forward reaction is exo-ergic and the reverse reaction endo-ergic by $(2E_{10}\delta\nu)$. The equation for a V-L process is

$$O_{(s)}(\nu) + \text{lattice} \underset{K_r}{\overset{K_f}{\rightleftharpoons}} O_{(s)}(\nu-1) + \text{lattice}^* \tag{5}$$

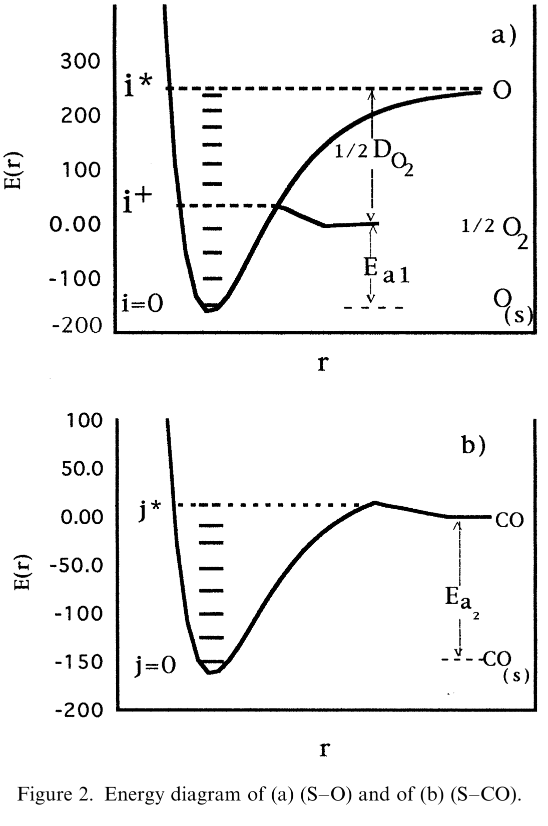

Figure 2. Energy diagram of (a) (S–O) and of (b) (S–CO).

where lattice* stands for an excited solid lattice, and similarly for $CO_{(s)}$. In this case

$$K_f = K_r \exp\left(\frac{E(\nu) - E(\nu-1)}{RT_s}\right) \tag{6}$$

and $K_f > K_r$ with the net result of driving the system towards a Boltzmann distribution.

Equations (3) and (5) are the two main scrambling processes of the vibrational energy pumped into the vibrational ladders of the adspecies by the corresponding chemisorption processes. The condition for attaining a quasi-steady-state non-equilibrium vibrational distribution is that rate coefficients $P_{f,r}$ and $K_{f,r}$ in equations (3) and (5) respectively, should obey the inequality

$$P_{f,r} \gg K_{f,r} \tag{7}$$

with $n = \sum n_\nu$ = total surface density of the adspecies. If inequality (7) is obeyed, the distribution functions at quasi-steady-state will be approximated by the Treanor vdf [5,6]

$$\ln\left(\frac{n_\nu}{n_0}\right) = -\frac{\nu E_{10}}{RT_s}\left[\frac{T_s}{T_1} - \delta(\nu-1)\right] \tag{8}$$

with

$$T_1 = (E_{10}/R\ln(n_0/n_1)) > T_s \tag{9}$$

measuring the over-population (n_1/molecule cm^{-2}) of level $\nu = 1$ with respect to a Boltzmann distribution. Equation (7) coincides with a Boltzmann vdf when $T_1 = T_s$. The Treanor vdf exhibits a minimum occurring at $\nu_{min} = (T_s/2\delta T_1) + \frac{1}{2}$. The shape of a Treanor distribution at given T_s is thus determined by the ratio (T_s/T_1); the smaller this ratio the larger the deviation from a Boltzmann distribution. This is well illustrated by the curves of figure 3 at same T_s but different (T_s/T_1). Notice, *e.g.*, that the relative population of the upper vibrational level changes by ~80 orders of magnitude, at $T_s = 300$ K, on going from a Boltzmann distribution, $(T_s/T_1) = 1$, to $(T_s/T_1) = 0.15$.

The possibility of reaching quasi-steady-state conditions characterized by non-Boltzmann vibrational distribution functions of the adspecies is therefore

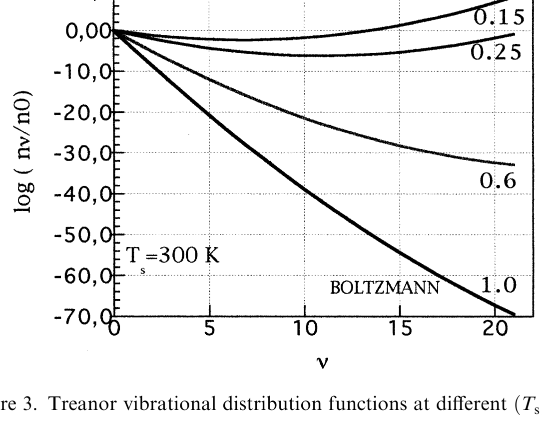

Figure 3. Treanor vibrational distribution functions at different (T_s/T_1).

bound to the existence of efficient processes of anharmonic vibration–vibration up-pumping in the adlayer, equation (3), and the validity of inequality (7). These conditions represent a crucial point of the model, and one should refer to refs. [2,3] for an analysis of the problems involved. The results of this analysis can be summarized as follows:

1. An estimate [2] of V-V rates, Pn s^{-1}, gives values between 10^{13} and 10^{8}, indicating that V-V transfer processes can be quite efficient in mobile adlayers.
2. Advanced experimental techniques and theoretical treatments have been utilized in recent times to evaluate vibrational relaxation times $\tau = K^{-1}$ of adspecies on solid surfaces (see [2] for references). Reported values of τ are in the 10^{-2}–10 ns range, depending on adsorbate, surface nature and conditions, with the corresponding K s^{-1} in the range 10^{11}–10^{8}.
3. The time scale of a catalytic reaction is, in the present model, unrelated with the time scales of V-V and of V-L processes. In fact, a simplified kinetic analogue can be written as

$$A_0 \underset{\tau_2^{-1}}{\overset{\tau_1^{-1}}{\rightleftharpoons}} A^* \xrightarrow{\tau_3^{-1}} C, \qquad \tau_1, \tau_2 \ll \tau_3$$
$$\mathrm{d}C/\mathrm{d}t = A^*/\tau_3 = (A_0/\tau_3)(\tau_2/\tau_1) \tag{10}$$

where A_0 and A^* are surface species in the ground or in the upper vibrational state respectively, C is a product species, τ_1^{-1} and τ_2^{-1} are probabilities per unit time for the occurrence of the process of vibrational excitation (Treanor up-pumping) and of de-excitation (vibrational relaxation to the solid lattice) respectively, and τ_3^{-1} is the probability per unit time of formation of C from the excited adspecies A^*.

The reaction rate $\mathrm{d}C/\mathrm{d}t$ is therefore related to the ratio, *not* to the absolute values of τ_1^{-1} or τ_2^{-1}. It should be emphasized that it is precisely the introduction of the up-pumping mechanism in the adlayer (equation (3)) that allows for a deviation from Boltzmann equilibrium. In fact, in the absence of process (3), over-populations of upper levels would decay to Boltzmann values in times much shorter than typical turnover times of catalytic reactions.

The reader should refer to ref. [10] for an extended analysis of the possibility of utilization of exo-ergic steps for the acceleration of successive energy-demanding steps in a surface reaction scheme.

In the model proposed in ref. [2], surface coverage is finite, and quasi-steady-state vdfs of the adsorbates are non-Boltzmann and approximated by Treanor or by Treanor-like distributions. In order to achieve these conditions, chemisorption kinetics was discussed in refs. [2,3] capable of both creating a finite surface coverage in a finite time and leading to a quasi-steady-state defined by non-equilibrium vdfs. This requires an initial process with $\mathbf{K} = (K/Pn) \gg 1$, *i.e.*, Boltzmann *initial* conditions, progressively shifting to $\mathbf{K} = (K/Pn) \ll 1$, thus allowing for the attainment of non-equilibrium quasi-steady-state conditions. Possible reasons for this shift have been considered in refs. [2,3].

Within this framework vibrational distribution functions of $\mathrm{O_{(s)}}$ and of $\mathrm{CO_{(s)}}$ will be approximated by Treanor equation (8), with the reasonable assumption of (T_s/T_1) common to both distributions.

2.1. *The LH* mechanism*

A Langmuir–Hinshelwood mechanism involving vibrationally excited adspecies (denoted LH* in refs. [3,4]) requires the rate-determining step

$$\mathrm{CO_{(s)}} + \mathrm{O_{(s)}} \Rightarrow \mathrm{CO_{2(g)}}$$

to be written as

$$\mathrm{CO_{(s)}}(j) + \mathrm{O_{(s)}}(i) \xrightarrow{K(i,j)} \mathrm{CO^*_{2(g)}}\langle i,j\rangle + 2S \tag{11}$$

i.e., as a reaction between the adspecies (S–CO) in its jth vibrational level and the adspecies (S–O) in its ith level, giving a vibrationally, rotationally and translationally excited gaseous $\mathrm{CO^*_{2(g)}}$ molecule. The $\langle i,j\rangle$ symbol means that $\mathrm{CO^*_{2(g)}}\langle i,j\rangle$ originates from the encounter of two adspecies in their ith and jth states respectively.

The rate of reaction (11) should be written

$$\frac{\mathrm{d}n^*_{\mathrm{CO_{2(g)}}}\langle i,j\rangle}{\mathrm{d}t} = K(i,j)n_1(i)n_2(j) \tag{12}$$

with $n_1(i)$ and $n_2(j)$ the surface densities (molecule cm^{-2}) of $\mathrm{O_{(s)}}$ and of $\mathrm{CO_{(s)}}$ respectively, The *total* rate of production of $\mathrm{CO_{2(g)}}$ will then be given by

$$\frac{\mathrm{d}n_{\mathrm{CO_{2(g)}}}}{\mathrm{d}t} = \sum_{i,j} K(i,j)n_1(i)n_2(j) \tag{13}$$

and the mole fraction in the gas phase of $\mathrm{CO^*_{2(g)}}\langle i,j\rangle$ molecules will be

$$\frac{n\mathrm{CO_{2(g)}}^*\langle i,j\rangle}{n_{\mathrm{CO_{2(g)}}}} = \frac{K(i,j)n_1(i)n_2(j)}{\sum_{i,j} K(i,j)n_1(i)n_2(j)}. \tag{14}$$

The consequence of the presence of an activation energy $E^{\#}$ for the formation of the product $\mathrm{CO_{2(g)}}$ from $\mathrm{CO_{(s)}}$ and $\mathrm{O_{(s)}}$ (figure 1) is that $\mathrm{d}n^*_{\mathrm{CO_{2(g)}}}\langle i,j\rangle/\mathrm{d}t$, as given by equation (12), becomes appreciable only for (i,j) couples satisfying the condition

$$[E_1(i) + E_2(j)] \geq E^{\#}. \tag{15}$$

The sum over the (i,j) couples satisfying constraint (15) will be denoted $\sum^{\#}_{i,j}$ and contains a *lower cut-off*.

With $P_1(i) = n_1(i)/n_1(0)$, $P_2(j) = n_2(j)/n_2(0)$, $\sum n_1(i) = n_1$, $\sum n_2(j) = n_2$, where n_1 is the total surface density of the (S–O) species, n_2 is the total surface density of (S–CO) and, to a first approximation, $K(i,j) = \bar{K}$, independent of i,j *for couples satisfying* *condition* (15), equation (13) becomes [4]

$$\frac{\mathrm{d}n_{\mathrm{CO}_{2(\mathrm{g})}}}{\mathrm{d}t} = \bar{K}\left[\frac{\sum^{\#}_{i,j} P_1(i)P_2(j)}{\sum_{i,j} P_1(i)P_2(j)}\right](n_1n_2) = k(n_1n_2) \quad (16)$$

with

$$k = \bar{K}\left[\frac{\sum^{\#}_{i,j} P_1(i)P_2(j)}{\sum_{i,j} P_1(i)P_2(j)}\right] = \bar{K}\Pi(E^{\#}, T_{\mathrm{s}}, (T_{\mathrm{s}}/T_1)) \quad (17)$$

a function of $E^{\#}$, T_{s}, (T_{s}/T_1).

Equation (14) is the starting point for calculating the total energy distribution functions of product molecules. Hyperthermal distributions of product $\mathrm{CO_2}$ formed in the heterogeneous oxidation of CO by either oxygen atoms or molecules have been fitted in ref. [4] starting from equation (14). A similar equation was utilized in ref. [3] in fitting non-Boltzmann distributions of HD molecules formed in abstraction reactions of chemisorbed D(H) by impinging H(D) atoms, or of $\mathrm{H_2}$ molecules in the heterogeneous recombination of H-atoms.

3. Non-equilibrium *versus* Boltzmann rate constants

In the case of heterogeneous isotope exchange reactions of diatoms (approximated in ref. [2] by a single species system), the steady-state relationship between adsorption and desorption rates in the dissociative chemisorption of diatom A_2, $A_2 \Leftrightarrow 2A_{(\mathrm{s})}$ is

$$J_{\mathrm{ads}} = Zn^{*2} \quad (18)$$

with the total flux J_{ads} (molecule $\mathrm{cm^{-2}\,s^{-1}}$) of adsorbing atoms given by

$$J_{\mathrm{ads}} = \tfrac{1}{2}\bar{c}_{\mathrm{g}}n_{\mathrm{g}}p_{\mathrm{s}}(1-\sigma)^2 = J(1-\sigma)^2 \quad (19)$$

where $\bar{c}_{\mathrm{g}}$ and n_{g} are the mean velocity and density respectively of A_2 in the gas phase, p_{s} is the sticking probability [11,12], and $\sigma = n/N$ is the fractional area occupied by adsorbed species (N, total density of adsorption sites).

In the treatment of heterogeneous isotope exchange reactions of ref. [2], desorption is assumed to occur at each encounter of two adatoms, both in their upper vibrational state ν^* ($\nu^* = i^+$ in figure 2(a)), so that the rate of desorption is given by Zn^{*2}, where n^* is the surface density of adspecies with vibrational quantum number ν^* and Z is a two-dimensional collision number of the order of $d\bar{c}_{\mathrm{s}}$, with d the collision diameter (of the order of $10^{-8}\,\mathrm{cm\,mol^{-1}}$) and $\bar{c}_{\mathrm{s}}$ the average two-dimensional velocity of the adspecies on the surface ($\mathrm{cm\,s^{-1}}$). Equations (18) and (19) give

$$\left(\frac{n^*}{n}\right)^2 = \left(\frac{J(1-\sigma)^2}{Zn^2}\right) \quad (20)$$

and, from Treanor equation (8) (when $n_0 \approx n$) [3],

$$\frac{T_{\mathrm{s}}}{T_1} = \delta(\nu^*-1) - \left(\frac{RT_{\mathrm{s}}}{2\nu^*E_{01}}\right)\ln\left(\frac{J(1-\sigma)^2}{Zn^2}\right) \quad (21)$$

relating (T_{s}/T_1) to T_{s}, to the intensity $J(1-\sigma)^2$ of the adsorption process populating the upper vibrational level ν^* of the (S–A) species, to surface coverage n, to ν^*E_{01} and to the two-dimensional collision number Z (see figure 4). The second-order rate constant of the surface process k is given by $kn^2 = Zn^{*2}$, and the "dimensionless non-equilibrium rate constant"

$$\kappa_{\mathrm{NE}} = \frac{k}{Z} = \left(\frac{n^*}{n}\right)^2$$

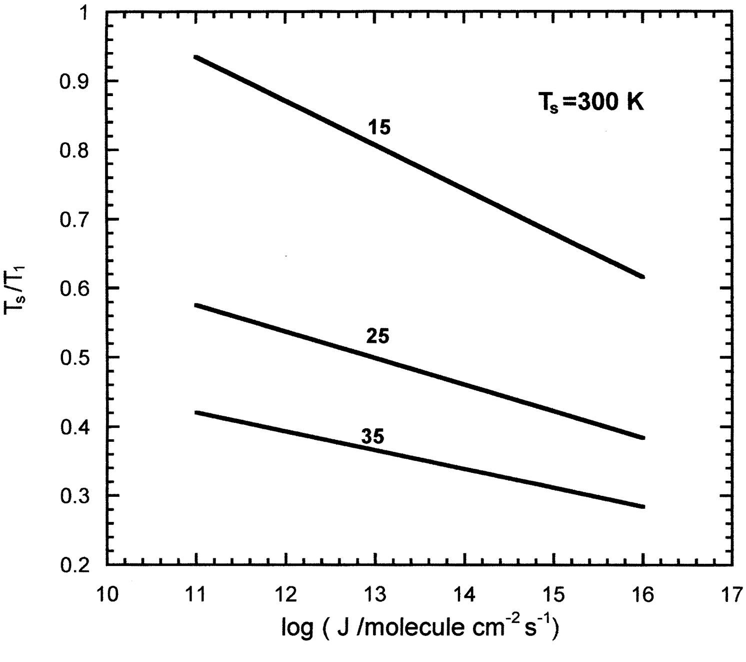

Figure 4. The ratio (T_{s}/T_1) plotted against the logarithm of the adsorption flux, J/molecule $\mathrm{cm^{-2}\,s^{-1}}$, equation (21), for various E_{01} ($\mathrm{kJ\,mol^{-1}}$).

is, according to equation (20),

$$\kappa_{\mathrm{NE}} = \frac{J(1-\sigma)^2}{Zn^2}. \tag{22}$$

It follows from equation (21) that, under non-equilibrium conditions, the shape of the vdf, which according to equation (8) is defined by (T_s/T_1), is determined, at given n, by the rate of the chemisorption process. This result is typical of non-equilibrium systems of the kind one is considering and directly follows from the solutions of master equation (9) of ref. [2]. It should be compared with the situation in systems in Boltzmann equilibrium where the fractional population (n^*/n) is *solely* determined, at T_s, by the Boltzmann factor $\exp(-E(\nu^*)/RT_s)$.

In Boltzmann equilibrium, equation (18) should be written as

$$J_{\mathrm{ads}} = Zn^{*2} = Zn^2 \exp(-2E(\nu^*)/RT_s) \tag{18$'$}$$

and the "dimensionless equilibrium-rate constant" is

$$\kappa_{\mathrm{B}} = \exp(-2E(\nu^*)/RT_s),$$

independent of J_{ads} and of n, in contrast to the non-equilibrium κ_{NE} of equation (22).

In the scheme of ref. [2], $E(\nu^*) = \nu^* E_{01}[1 - \delta(\nu^* - 1)]$ gives, approximately, the depth of the energy well of the (S–A) species (figure 2(a)). With $E_1(\nu^*) = 8\,\mathrm{kJ\,mol^{-1}}$, $E_2(\nu^*) = 40\,\mathrm{kJ\,m^{-1}}$, one obtains, at 400 K, $(\kappa_{\mathrm{B}_2}/\kappa_{\mathrm{B}_1}) = 1.7 \times 10^5$. The corresponding ratio in a non-equilibrium system $(\kappa_{\mathrm{NE}_2}/\kappa_{\mathrm{NE}_1})$ is, *a priori*, undetermined and might well be equal to 1 if, *e.g.*, both J and n were the same for catalyst 1 and 2 (equation (22)).

The case of carbon monoxide oxidation is more complex in that it involves various quasi-steady states

$$\begin{aligned} 2\mathrm{CO_{(s)}} &\Leftrightarrow \mathrm{CO_{(g)}} + \mathrm{CO_{(s)}}, \\ 2\mathrm{O_{(s)}} &\Leftrightarrow \mathrm{O_{2(g)}}, \\ \mathrm{CO_{(s)}} + \mathrm{O_{(s)}} &\Leftrightarrow \mathrm{CO_{2(s)}} \Leftrightarrow \mathrm{CO_{2(g)}}. \end{aligned} \tag{23}$$

Let us simplify the problem as follows: with reference to figures 2(a) and 2(b) one writes

$$\begin{aligned} J_{\mathrm{CO}} &= Z_{\mathrm{CO,CO}} n_2(j^*)^2 + Z_{\mathrm{CO,O}} n_2(j^*) n_1(i^+), \\ J_{\mathrm{O}} &= Z_{\mathrm{O,O}} n_1(i^+)^2 + Z_{\mathrm{CO,O}} n_2(j^*) n_1(i^*), \end{aligned} \tag{24}$$

with J_{CO} and J_{O} the total fluxes of *adsorbing* CO and O, respectively.

The simplification consists in writing the rate of $\mathrm{CO_{2(g)}}$ production as $Z_{\mathrm{CO,O}}[n_2(j^*)n_1(i^+)]$, whereby assuming that this reaction occurs at every encounter between $\mathrm{CO_{(s)}}(j^*)$ and $\mathrm{O_{(s)}}(i^+)$, *i.e.*, between adspecies *both* in their upper vibrational state. This is not rigorous, as discussed in the previous section, but can be taken as a heuristic approximation. Let us then write, as a further reasonable approximation, $\bar{Z} = (Z_{\mathrm{CO,CO}} + Z_{\mathrm{O,O}} + Z_{\mathrm{CO,O}})/3$, and transform equation (24) into

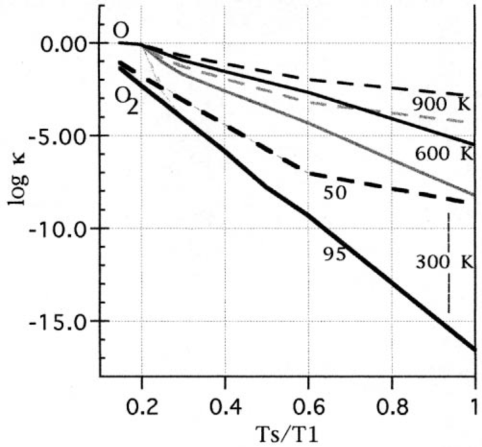

Figure 5. Dimensionless non-equilibrium rate constants κ for CO oxidation in atomic oxygen, calculated at $T_s = 300$, 600, 900 K and $E^{\#} = 50\,\mathrm{kJ\,mol^{-1}}$ (dashed lines) and $E^{\#} = 95\,\mathrm{kJ\,mol^{-1}}$ (solid lines), *versus* (T_s/T_1). Thick lines refer to the reaction in molecular oxygen at 300 K.

$$\begin{aligned} J_{\mathrm{CO}} &= \bar{Z}[n_2(j^*)^2 + n_2(j^*)n_1(i^+)] \\ J_{\mathrm{O}} &= \bar{Z}[n_1(i^+)^2 + n_2(j^*)n_1(i^+)] \end{aligned} \tag{24$'$}$$

from which one obtains, after some manipulation,

$$\left(\frac{n_1(i^+)n_2(j^*)}{n_1 n_2}\right) = \left(\frac{J_{\mathrm{CO}} J_{\mathrm{O}}}{J_{\mathrm{CO}} + J_{\mathrm{O}}}\right) \frac{1}{\bar{Z}(n_1 n_2)} \tag{25}$$

to be compared with equation (22) leading to the same basic result: the product of the fractional populations of upper vibrational levels of the adspecies is not related to Boltzmann factors but to the flux of adsorbing species $(J_{\mathrm{CO}} J_{\mathrm{O}}/J_{\mathrm{CO}} + J_{\mathrm{O}})$ and to $(n_1 n_2)$. One can now drop the above heuristic approximation and analyze the dependence of the dimensionless rate constant for CO oxidation κ on $E^{\#}$, T_s and (T_s/T_1) by solving equation (17) numerically.

Figure 5 shows $\log\kappa$, as calculated from equation (17) for the reaction in atomic oxygen, plotted against (T_s/T_1) at different T_s and two different values of $E^{\#}$ ($95\,\mathrm{kJ\,mol^{-1}}$ (solid lines) and $50\,\mathrm{kJ\,mol^{-1}}$ (dashed lines)); $\log\kappa$ at 300 K for the reaction in molecular oxygen is also shown for comparison (thick lines).

The temperature dependence of $\log\kappa$ derived from figure 5, at constant (T_s/T_1), can be fitted by Arrhenius equations with slopes decreasing with decreasing (T_s/T_1). From these slopes one obtains the "non-equilibrium activation energies" $E^{\#}_{\mathrm{NE}}$ which have been plotted in figure 6 *versus* (T_s/T_1).

Figures 5 and 6 allow a comparison to be made between non-equilibrium and Boltzmann dimensionless rate constants.

The ratio between rate constants corresponding to "true" activation energies $E^{\#}$ of 50 and of $95\,\mathrm{kJ\,mol^{-1}}$ are the following for Boltzmann vdfs $((T_s/T_1) = 1)$: $(\kappa_{50}/\kappa_{95}) = 7 \times 10^7$, 8×10^3, 4×10^2 at 300, 600 and 900 K respectively.

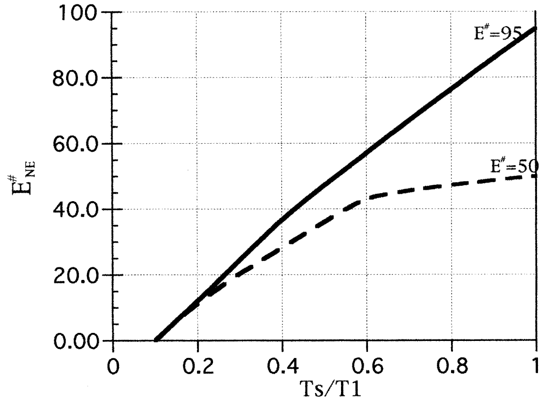

Figure 6. Non-equilibrium activation energy $E^{\#}_{\mathrm{NE}}$ *versus* (T_s/T_1) for $E^{\#} = 95\,\mathrm{kJ\,mol^{-1}}$ (solid line) and $E^{\#} = 50\,\mathrm{kJ\,mol^{-1}}$ (dashed line).

At $(T_s/T_1) = 0.3$ these ratios become $(\kappa_{50}/\kappa_{95}) = 7$, 3, 1.5.

Values of κ for the reaction in atomic oxygen approach the upper limit of 1 at $(T_s/T_1) < 0.15$, at all temperatures. This behavior is reflected in the data of figure 6, which show the expected decrease of $E^{\#}_{\mathrm{NE}}$ with decreasing (T_s/T_1).

The interpretation of these results is straightforward; it simply reflects the increased populations of (i,j) couples satisfying constraint (15) and connected with a decrease of (T_s/T_1) in the Treanor vdfs of the (S–CO) and (S–O) surface species. The influence of T_s on these populations is therefore also expected to decrease with a decrease of (T_s/T_1), and κ becomes temperature-independent ($E^{\#}_{\mathrm{NE}} = 0$) at values of (T_s/T_1) of about 0.1 because essentially all (i,j) couples will now satisfy constraint (15) in the whole range of temperatures considered (300–900 K).

Another important observation stems from figure 5, namely that catalysts with widely different "true" activation energies $E^{\#}$ can exhibit an equal κ, at the same T_s, provided (T_s/T_1) is properly selected for each system (table 1 and figure 5).

In figures 5 and 6, Boltzmann rates represent but a limiting case, $(T_s/T_1) = 1$, of a more general non-equilibrium picture showing that two parameters, besides T_s, are now necessary to define the non-equilibrium rate constant κ, namely $E^{\#}$ and (T_s/T_1).

It should be remembered, as shown in refs. [3,4], that Treanor equation (8) is a suitable representation of a non-equilibrium vdf, but that vdfs other than equation (8) may be necessary for simulating non-equilibrium distributions under special conditions of vibrational pumping.

Equations (20), (21) and (25) show that, in the case of an isotope exchange reaction or in the heuristic model of carbon monoxide oxidation, (T_s/T_1) is rather simply related to the intensity of the adsorption processes populating the upper vibrational levels of the relevant adspecies, and that small (T_s/T_1) should be expected for large J. In the actual oxidation process the relationship between (T_s/T_1), J and n is more complex but, in any case, $(T_s/T_1) = F(J_x)$, a decreasing function of the J. Chemisorption of the reactants and the successive reaction steps on the surface, which are normally considered as independent from one another (one of them is rate-determining), actually become closely coupled in this non-equilibrium picture in that the adsorption flux J now controls the rate constants of successive steps *via* (T_s/T_1).

Table 1
Isokinetic values of $(T_s/T_1)_{E^{\#}}$ at various T_s.

	$\log\kappa$	$(T_s/T_1)_{95}$	$(T_s/T_1)_{50}$
$T_s = 300\,\mathrm{K}$	−7.0	0.46	0.61
	−5.0	0.35	0.45
$T_s = 600\,\mathrm{K}$	−3.0	0.45	0.57
$T_s = 900\,\mathrm{K}$	−2.0	0.50	0.63

One appreciates that the suggested presence of non-equilibrium vdfs, with their over-population of excited vibrational levels, actually defines a "hot atom" model. "Hot atoms" are here seen as mobile adspecies, with all their vibrational levels excited according to non-equilibrium Treanor or Treanor-like distribution functions. The original concept of "hot atom" reaction [13], has recently been utilized in kinetic schemes [14,15] and in Monte Carlo simulations [16]. In these treatments "hot atoms" are seen as one or as two species at correspondingly higher energies. In our model each excited vibrational level actually corresponds to a different "hot" species, as follows from equations (11)–(13). The proposed LH* scheme could then also be called a *multilevel* "hot atom" model.

4. Non-equilibrium rates and the "compensation effect"

Differentiation with respect to temperature of the total rate of $\mathrm{CO_{2(g)}}$ production

$$\mathbf{R} = \frac{\mathrm{d}n_{\mathrm{CO_{2(g)}}}}{\mathrm{d}t} = k(n_1 n_2),$$

in logarithmic form, gives

$$E = E^{\#}_{\mathrm{NE}}(E^{\#}) + RT^2\,\frac{\mathrm{d}\ln(n_1 n_2)}{\mathrm{d}T} \qquad (26)$$

relating the experimental, "apparent" activation energy E to the "non-equilibrium activation energy" of the process $E^{\#}_{\mathrm{NE}}$, in the case of non-equilibrium steady states, or to the "true" activation energy of the process $E^{\#}$ in the case of Boltzmann equilibrium in the adlayer. From the experiments one normally obtains $\mathbf{R}$ and E only, because both $(n_1 n_2)$ and $\mathrm{d}\ln(n_1 n_2)/\mathrm{d}T$ are, in most cases, not available.

Let us have a series of $1, 2, \ldots, n$ catalysts with experimental (apparent) activation energies $E_{1,2,\ldots,n}$ and corresponding blunt Arrhenius equations

$$\log \mathbf{R}_n = \log A_n - E_n/2.3RT_s \tag{27}$$

The long-debated "compensation effect" in heterogeneous catalysis, also known as the "Θ rule" (see [1,2] for references), consists of the observation that the pre-exponential term A_n can itself be a function of E_n of the kind

$$\ln A_n = \ln B + E_n/R\Theta \tag{28}$$

whereby

$$\mathbf{R}_n = B \exp\left[\frac{-E_n}{RT_s}\left(1 - \frac{T_s}{\Theta}\right)\right] \tag{29}$$

so that, at $T_s = \Theta$, $\mathbf{R}_n = B$, independent of E_n. "Compensation" implies that high values of the experimental activation energy E are "compensated" by correspondingly high values of the pre-exponential factor A so that, at the characteristic *isokinetic* temperature Θ, the catalysts investigated exhibit comparable rates and Arrhenius plots of different E_n merge at $\log \mathbf{R}_n(\Theta) = \log B$. At $T_s = \Theta$,

$$\mathbf{R}_1(\Theta) = \mathbf{R}_2(\Theta) = \cdots = \mathbf{R}_n(\Theta)$$

and

$$\begin{aligned}\kappa_1(\Theta)(n_1n_2)_1(\Theta) &= \kappa_2(\Theta)(n_1n_2)_2(\Theta) \\ &= \cdots = \kappa_n(\Theta)(n_1n_2)_n(\Theta).\end{aligned} \tag{30}$$

With Boltzmann rate constants, $\kappa_{B1} \neq \kappa_{B2} \neq \cdots \neq \kappa_{B_n}$ by orders of magnitude, except at $T_s = \infty$. With non-equilibrium rate constants we have just shown, on the contrary, that $\kappa_{NE_1} = \kappa_{NE_2} = \kappa_{NE_n}$, at a finite value of T_s, provided one selects isokinetic values of $(T_s/T_1)_1, (T_s/T_1)_2, \ldots, (T_s/T_1)_n$, *e.g.*, as in table 1. Therefore, the possibility exists that, $\kappa(\Theta)_{NE_1} = \kappa(\Theta)_{NE_2} = \kappa(\Theta)_{NE_n}$, and the validity of (30) then implies

$$(n_1n_2)_1(\Theta) = (n_1n_2)_2(\Theta) = \cdots = (n_1n_2)_n(\Theta), \tag{31}$$

i.e., at $T_s = \Theta$, the products of the surface densities of the two adspecies should merge to a $(n_1n_2)(\Theta)$ value common to all the catalysts of the series. In the case of the two isotope exchange reactions discussed in ref. [2] ($H_2 + D_2 = 2HD$ on pure and "doped" ZnO [17], and ${}^{16,16}O_2 + {}^{18,18}O_2 = 2{}^{16,18}O_2$ on various series of metal oxides [18]) this prediction (see also ref. [19]) was confirmed by *independent* data for chemisorption of H_2 on ZnO [20] and of O_2 on the metal oxides [18]. The amounts of H_2 adsorbed at $T_{ads} = 353$ K by the various ZnO catalysts [20] can reasonably be fitted by an equation of the kind

$$\ln(n_{T_{ads}})_n^2 = \ln(n_\Theta)^2 + \frac{(E - E^{\#})_n}{R}\left(\frac{1}{\Theta} - \frac{1}{T_{ads}}\right) \tag{32}$$

with n_Θ common to all the catalysts of the series, and $\Theta = 450$ K as derived from the isotope exchange data [17]. The same equation applies to the amounts of O_2 chemisorbed at $T_{ads} = 576$ K on a series of metal oxides, with $\Theta = 675$ K derived from the oxygen isotope exchange data [28].

Values of $\ln(n_{T_{ads}})_n^2$ calculated as a function of $(E - E^{\#})_n$, on the assumption of Boltzmann equilibrium, have been found to be totally incompatible with equation (32) (see figure 11 of ref. [2]). The general tacit assumption of Boltzmann equilibrium in the adlayer apparently leads to results incompatible with the observed simultaneous validity of equations (29) and (32). These equations do find, however, a rationale in the suggested existence of non-equilibrium conditions in the adlayer, under working conditions of the catalyst. It should be stressed that non-equilibrium is confined, in our model, to working conditions of a catalytic surface because the relevant adsorption processes must be intense enough to ensure a significant departure from Boltzmann vdfs.

From a general point of view, the information which can be derived from equation (29) is ambiguous because of the great uncertainties connected with both the experimental temperature coefficients E, which are, in general, only remotely connected with the "true" activation energies $E^{\#}$, and with the corresponding values of experimental pre-exponential factors A_n, which can vary by many (*e.g.*, 19) orders of magnitude within a series and fall short of any reasonable physical interpretation [1,2,21,22]. The validity of equation (29), which appears to be both genuine and general, in the sense discussed in the Appendix of ref. [2], is in any case relevant in that it shows its inconsistency with an equilibrium picture of a working catalytic surface and requires therefore an alternative approach. From the point of view of non-equilibrium vibrational kinetics in adlayers, the validity of the "Θ rule" represents, on the contrary, a significant "supporting case" because equation (29) can rather naturally be derived from a non-equilibrium model of the catalytic surface.

Other non-Boltzmann approaches to the "Θ rule" have appeared in the literature. Two of them should be cited [23,24, and previous work by these authors], which have been examined in a recent review on the isokinetic relationship [25].

5. Conclusions

Non-equilibrium vibrational kinetics in the adlayer, as developed in refs. [1–4] and further discussed in the present paper, provides a picture of a working catalytic surface which is different from that based on the current assumption of Boltzmann equilibrium.

An alternative definition of an active catalyst does in fact emerge from this discussion: the role of a heterogeneous catalyst remains that of providing an alternative reaction path by preliminary chemisorption of reactants in a form favoring their reactivity. This alternative path, however, is not necessarily characterized by a "true" activation energy $E^{\#}$ lower than that of the gas-phase reaction, as generally stated, but rather by the capability of the reactive gas–solid system of maintaining a quasi-steady state at the surface sufficiently removed from Boltzmann equilibrium at the working temperature of the catalyst. In fact, under non-equilibrium conditions, rates of surface reactions are characterized by the parameter (T_s/T_1), defining the shape of Treanor vibrational distribution functions, besides $E^{\#}$. As a consequence, reactions with widely different $E^{\#}$ can exhibit comparable reaction rates, at finite T_s, by proper selection of (T_s/T_1).

The suggested LH* model is a thermodynamic one in which vibrational distribution functions of the adspecies are defined by Treanor or by Treanor-like functions rather then by Boltzmann ones. This follows from the anharmonicity of the vibrational ladders of the adspecies and from their surface mobility. A Treanor up-pumping process (equation (3)) should then be duly taken into account; it can prevail in the presence of sufficiently intense adsorption events over-populating the upper levels of the various vibrational ladders, thus shifting the system towards non-equilibrium quasi-steady states. The proposed LH*, or multilevel "hot atom", model can fit hyperthermal energy distributions of gaseous product molecules leaving the catalytic surface, as discussed in [3,4]. In the present paper, and in refs. [1,2] we have shown how "compensation" in heterogeneous catalysis can be seen as a natural consequence of a non-equilibrium state of the catalytic surface under working conditions. This non-equilibrium state can be established, however, in the presence of an efficient vibrational up-pumping mechanism only.

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