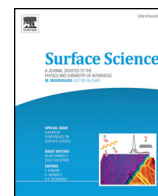




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Lateral interactions and non-equilibrium in surface kinetics

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ABSTRACT

Work modelling reactions between surface species frequently use Langmuir kinetics, assuming that the layer is in internal equilibrium, and that the chemical potential of adsorbates corresponds to that of an ideal gas. Coverage dependences of reacting species and of site blocking are usually treated with simple power law coverage dependences (linear in the simplest case), neglecting that lateral interactions are strong in adsorbate and co-adsorbate layers which may influence kinetics considerably.

My research group has in the past investigated many co-adsorbate systems and simple reactions in them. We have collected a number of examples where strong deviations from simple coverage dependences exist, in blocking, promoting, and selecting reactions. Interactions can range from those between next neighbors to larger distances, and can be quite complex. In addition, internal equilibrium in the layer as well as equilibrium distributions over product degrees of freedom can be violated. The latter effect leads to non-equipartition of energy over molecular degrees of freedom (for products) or non-equal response to those of reactants. While such behavior can usually be described by dynamic or kinetic models, the deeper reasons require detailed theoretical analysis. Here, a selection of such cases is reviewed to exemplify these points.

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1. Introduction

Surface reaction modelling widely uses Langmuir kinetics for individual steps. Coverage dependences are usually assumed to follow simple power laws, neglecting the possibility of attractive interactions among the adsorbed reactants, and taking repulsive interactions into account only via site blocking. Promoter and inhibitor actions, which mostly also are based on lateral interactions, are often considered as *ad hoc* effects. Furthermore, equilibrium with the gas phase, or at least quasi-equilibrium (i.e. equilibrium within the adsorbed layer), is mostly assumed. These approximations are often safe at low coverages, i.e. at comparatively high temperatures on the scale of the reaction energetics. But low temperature reaction conditions are very desirable, and at least under such conditions, these assumptions may well be incorrect. In the following, I want to examine evidence for the importance of these two aspects, lateral interactions and non-equilibrium effects, on the kinetics of some simple surface reactions.

Lateral interactions among like or dissimilar adsorbate species are well-known to abound and to have characteristic influences on the behavior of the coupled system. They lead to ordered adsorbate structures, influence the electronic and vibrational structure of the layers, and have profound effects on adsorption, desorption, and reaction kinetics via coverage-dependent energies and entropies of adsorption. Repulsive and attractive interactions can go beyond pairwise to trio and even higher interactions, and can be quite long-ranged. In terms of the underlying physics, they can be based on electrostatic (dipole or multi-pole) through space or through substrate (electronic or elastic) effects. They are active

even at coverages below, or at temperatures above, those necessary to form observable overstructures. Thus, they cannot be neglected even there, since they influence the distributions of adsorbates and co-adsorbates over sites, making them different from random. Also, promoter and inhibitor influences are due to lateral interactions which can go beyond simple site blocking. The strong influences of alkali promoters and of other co-adsorbates, which modify the charge transfer between adsorbates and substrates, change the density of states at the Fermi level and shift molecular orbitals are well-known and widely used in practical catalysis. To consider them as lateral interactions of co-adsorbates can deepen their understanding.

Non-equilibrium effects can come in various forms. Since any reaction with finite rate is a non-equilibrium process, it is not surprising that not infrequently it cannot be fully described by the equilibrium energetics modified by a kinetic factor such as the sticking coefficient (see below). Deviations from quasi-equilibrium can be seen when the reacting adsorbate or co-adsorbate layer are not in internal equilibrium during reaction, due to 2D diffusion or to other redistribution effects. This can lead to unusual kinetics, necessitating the modification of a simple ansatz. Such situations are indicated by reaction rates which are not just functions of temperature and partial pressures (or average surface coverages). They become easily observable through kinetics, which depend on the way the reaction is carried out, or on the prehistory, i.e. the preparation method of the starting system.

Another non-equilibrium effect can arise from the dynamics of the adsorption/desorption or reaction processes. In cases of non-equipartition of energy over the molecular degrees of freedom of reaction products

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(e.g., in reactive desorption), the principle of detailed balance requires that the same selection of non-equipartition also pertains to adsorption. The latter will then selectively enhance or suppress reactions for certain modes. It cannot be excluded that such effects influence surface reactions, even though it applies strictly only under equilibrium. An obvious extreme example is that of surface photochemistry, which induces such non-equipartition effects. It will not be included in the present discussion.

This paper is based on a talk given at the symposium honoring Robert J. Madix at the occasion of his receiving the G.A. Somorjai reward of the American Chemical Society (March 2010, San Francisco). It has not been published elsewhere and appears as a fitting tribute to Bob who has been my highly appreciated colleague and friend for almost 50 years, with whom I discussed questions related to the topics in this paper very early on, and who has pioneered the use of TPRS (temperature programmed reaction spectroscopy) [1] for the analysis of surface reactions. It will present examples for all the mentioned effects, taken from the work of my group over several decades.

First, I will give a short summary of approaches to the kinetics of surface reactions, as I see them. Then, I will briefly sketch a number of examples for each of the complicating factors mentioned.

2. Basic kinetics

The basic connections between equilibrium and rate processes on surfaces have been well known for many decades, and a large number of studies are contained in the literature. Since this is not a review of the field but a selective collection of case studies of possible interest for other applications, no attempt will be made to give a comprehensive account of the literature, and it may be permissible to concentrate on our work. Surprisingly, the basics are not always appreciated; quite often, very simplistic models (e.g., coverage independent energy and pre-exponentials for desorption, the latter often set to of 10^{13} s^{-1} , which may have been justified in the early days [2,3]), are still applied frequently without justification. So, a short summary will be given first for the simplest case which is partly contained in a 40-year-old paper [4], with later expansions and detailed discussion [5,6].

The usual parameterization of a rate by a Polanyi–Wigner equation gives:

$$\text{rate} = f(N, T) = f(N) \cdot k_0 \cdot \exp(-E/kT) \quad (1)$$

The simplest reactive step is desorption of an adsorbate species; so

$$r_{\text{des}} = -dN_a/dt = k_m \cdot N_a^m = N_a^m \cdot k_0 \cdot \exp(-E_{\text{des}}/kT) \quad (2)$$

or

$$r_{\text{des}} = -d\theta/dt = k_m \cdot \theta^m = \theta^m \cdot k_0 \cdot \exp(-E_{\text{des}}/kT) \quad (3)$$

However, in general, no such separation is possible; at least E and k_0 are usually functions of coverage.

Adsorption–desorption equilibrium with the gas phase, with or without any reaction steps, contains thermal and chemical equilibrium: temperature T and all chemical potentials μ_i are equal for all components and in all phases. For the simplest case of adsorption–desorption equilibrium (leaving out other reaction steps) of a single species (“1 – 1” adsorption–desorption)

$$A_{\text{ad}} \rightleftharpoons A_{\text{gas}} \quad (4)$$

it is described by

$$\begin{aligned} (N_{\text{ad}}/A)/(N_{\text{g}}/V) &= n_{\text{ad}}/n_{\text{g}} = K_{\text{eq}} = \exp(-\Delta F_0/RT) \\ &= (\mathcal{F}_{\text{ad}}/\mathcal{F}_{\text{g}}(3D)) \cdot \exp(-\Delta E_{\text{eq}}/RT) \end{aligned} \quad (5)$$

(where the N are the particle numbers and the n their densities, K_{eq} the equilibrium constant, ΔF_0 the standard free energy change, the \mathcal{F} the

products of partition functions for gas and surface species, ΔE_{eq} the standard inner energy change, T the temperature, and R the gas constant).

On the other hand, in equilibrium, the rates of adsorption and desorption must be equal: so that

$$\begin{aligned} r_{\text{ad}} &= s(\theta, T) \cdot n_{\text{g}} \cdot v_{\text{th}}/4 = s(\theta, T) \cdot n_{\text{g}} \cdot (kT/2\pi m)^{1/2} \\ &= n_{\text{ad}} \cdot k_0 \cdot \exp(-E_{\text{des}}/RT) = r_{\text{des}} \end{aligned} \quad (6)$$

(with s the sticking coefficient, θ the coverage, v_{th} the average thermal velocity, k the Boltzmann constant, m the particle mass, k_0 the desorption pre-exponential, r_{des} the rate of desorption, and E_{des} the desorption energy).

With Eq. (5), this can be rewritten as

$$k_0 = s(\theta, T) \cdot (kT/2\pi m)^{1/2} \cdot (\mathcal{F}_{\text{g}}/\mathcal{F}_{\text{ad}}) \cdot \exp(-(E_{\text{eq}} - E_{\text{des}})/RT) \quad (7)$$

(where the thermodynamic quantities are also coverage- and temperature-dependent), and for nonactivated adsorption ($E_{\text{eq}} = E_{\text{des}}$) simplifies to

$$k_0 = s(\theta, T) \cdot (kT/2\pi m)^{1/2} \cdot (\mathcal{F}_{\text{g}}/\mathcal{F}_{\text{ad}}). \quad (8)$$

Thus, the intrinsic rate of desorption is the product of a dynamical factor, the sticking coefficient, and the equilibrium thermodynamic factor from Eq. (7) [5,7]. More unified and detailed treatments which contain lattice gas models of lateral interactions have been developed [8,9] and applied to simple cases in which a large data base makes comparison sensible [10,11]. Stochastic distributions during reaction under the influence of various lateral interactions are calculated using a Markovian master equation with phenomenological lattice gas Hamiltonian with n -site correlators. Inclusion of non-equilibrium situations is possible by introducing two time scales [12]. These treatments can also be used to directly calculate thermal desorption spectra for comparison with experiment, avoiding to impose any parametrisation form. Some uses of such modelling will be mentioned in the case studies described below.

$$\begin{aligned} \text{As } v_{\text{th}} &= (8kT/\pi m)^{1/2} \cdot \mathcal{F}_{\text{g}}(3D) = f_{\text{tr}}^3 \cdot f_{\text{rot}} \cdot f_{\text{vib}} \text{ with } f_{\text{tr}}(1D) \\ &= (2\pi mkT)^{1/2}/h \end{aligned} \quad (9)$$

(with h Planck's constant),

Eq. (8) can be rewritten

$$r_{\text{des}} = s(\theta, T) \cdot n_{\text{ad}} \cdot (kT/h) \cdot (\mathcal{F}_{\text{g}}(2D)/\mathcal{F}_{\text{ad}}) \cdot \exp(-E_{\text{eq}}/RT) \quad (10)$$

and

$$k_0(\text{des}) = s(\theta, T) \cdot (kT/h) \cdot (\mathcal{F}_{\text{g}}(2D)/\mathcal{F}_{\text{ad}}) \quad (11)$$

These treatments can be generalized to any reaction step.

We can also apply transition state theory, which is a quasi-equilibrium treatment as well. For the pre-exponential of the rate of desorption for non-activated adsorption we then get

$$k_0(\text{des}) = \kappa \cdot (kT/h) \cdot (\mathcal{F}_{\text{g}}/\mathcal{F}_{\text{ad}}). \quad (12)$$

(where κ is the transmission factor). This expression is seen to be equivalent to the equilibrium treatment (Eq. (11)) if $s = \kappa$. So again the desorption rate can be factored into an energetic equilibrium part and a dynamic factor which here is the transmission factor. It should be noted, however, that the equilibrium treatment contains the full flexibility of the temperature and coverage dependent sticking coefficient, contrary to the TST treatment.

The transition state approach, with full inclusion of statistical factors, has in fact been used for catalytic reactions early on [13].

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