

## Dynamic theory of adsorption on surfaces undergoing self-similar reconstruction

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A rate equation, which takes explicitly into account the surface reconstruction phenomena occurring (reversibly or irreversibly) while adsorption or desorption proceeds, is proposed. The equation contains a few free parameters which specify the adsorption and desorption rate constants, and the reconstruction and irreversibility degrees of the process. A complete qualitative study of the solutions of the rate equation for two kinds of reversible and self-similar reconstruction is given.

### 1. INTRODUCTION

That a surface may undergo during adsorption (and especially chemisorption) even large reconstruction (in this way behaving like a ‘flexible’, rather than hard, surface [1]) has been well known for many years. Many activation-deactivation phenomena observed in catalysis are indeed interpreted just in terms of adsorption-induced reconstruction. A classical example is provided by the heterogeneously catalyzed synthesis of ammonia via the Haber-Bosch process, whose catalyst is a mixed oxide of iron, aluminum, calcium and potassium: In reaction conditions  $\text{Fe}_3\text{O}_4$  is reduced to elemental Fe. Even though the dominantly active component of the catalyst is the *crystalline*  $\alpha$  phase of iron, the remarkable longevity of the catalyst (the freshly prepared one having almost the same activity as one that had been continuously used for 14 years [2]) is explained in terms of “quasi-*liquid* nature of the catalyst, since such material would be capable of constant regeneration of surface atoms” [3], contradiction (evidenced by the emphasized words) that may be removed in terms of surface reconstruction.

The origin of adsorption-induced surface reconstruction is the adsorption energy: the higher it is (compared with the cohesion energy), the larger is the driving force for surface reconstruction. However, the actual amount of surface

reconstruction is not directly related to the energy released during adsorption, but rather to the detailed mechanism through which the energy excess is imparted to the solid following adsorption: If surface reconstruction is simply connected with the thermodynamics of the adsorbate-adsorbent system, then it is closely related to the spontaneous roughening of clean surfaces; otherwise, when surface reconstruction is connected with the detailed mechanism through which the energy excess resulting from adsorption is distributed among the adsorbent atoms, this phenomenon is contrasted by spontaneous smoothing [4].

The importance of adsorption-induced reconstruction is well known for inorganic, organic as well as biological adsorbents. Though this phenomenon has occasionally been considered with specific models (for instance, to describe allosteric effects in adsorption [5], heterogeneity, hysteresis and allostercity in water adsorption on proteins [6], conformational changes upon adsorption of gases on polymers [7, 8], or dimple formation on metal surfaces upon physisorption [9]), no particular *model* has however been demonstrated to be so ductile as to generate a general *theory*<sup>1</sup> for the description of *adsorption-induced reconstruction*. A possible reason for this lack is the fact that the most ductile theory of adsorption-desorption (hereinafter collectively referred to as AD-sorption) phenomena, (i.e. the Langmuir theory), is constructed assuming explicitly that *the surface does not undergo reconstruction*.

AD-sorption equilibrium is usually described on statistico-mechanical bases formulating suitable models for it. The equilibrium properties can be exported to describe kinetics using Ward's statistical rate theory [10-12]. In this theory, the exchange rate in any condition from one phase to another is written as a function of the difference of chemical potentials in the two phases (and thus is a thermodynamic quantity) times the exchange rate between them under equilibrium. The ability of Ward's approach to account for AD-sorption phenomena has recently been explored by Rudziński and coworkers [13-16]. The advantages of the statistical rate theory over a true kinetic description of AD-sorption are that the equilibrium properties are known much more accurately than adsorption and desorption rates and that all the knowledge on the thermodynamic state of the system (in particular, on the non-ideality of the gas phase) can be imported in the kinetic theory. The obvious disadvantage of the statistical rate theory is that it requires a knowledge of the equilibrium state

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<sup>1</sup> The word 'theory' is used to denote a general scheme for the description of a large class of phenomena (in this sense I speak of 'Langmuir theory of localized adsorption' or 'BET theory of multilayer adsorption'). The word 'model' is used to denote a scheme for the understanding of a given empirical relationship (in this sense I speak of 'Landsberg model for the Elovich equation') or the description of particular systems. Needless to say, the border between theory and model is confused and a model can inductively be used for the foundation of a theory.

that in some cases (and especially in most of cases considered in this work) may not exist (in the sense that the time evolution of the system is only limited by factors extraneous to AD-sorption, like the bound amount of matter or space available for the growth). If one is interested not only in describing equilibrium, but also in understanding when it is possible, one necessarily needs a dynamical description of the system and in the long run limit her or his attention to the equilibrium states of the dynamic system, when they exist<sup>2</sup>.

This work is devoted to reformulate Langmuir's dynamic theory to account for surface reconstruction phenomena occurring while AD-sorption proceeds.

## 2. THE LANGMUIR THEORY

Formulated in 1916, the Langmuir theory of AD-sorption equilibrium and kinetics has remained unrivalled during the 20th century for its simplicity, elegance, and ductility [18].

### 2.1. Basic assumptions and formal development

The Langmuir theory  $\mathcal{L}$  describes adsorption as the formation of filled surface sites (denoted with  $\bullet$ ) by the reaction of empty surface sites (denoted with  $\circ$ ) with gas-phase molecules  $M$  and desorption by the opposite process.

#### 2.2.1. The axioms of the Langmuir's theory

The Langmuir theory applies to localized AD-sorption and is based on the following assumptions:

**L1 (One-molecule/one-site)** *A site is filled by reaction with one and only one molecule; the extrasite space is unavailable for adsorption.*

**L2 (Absence of intermolecular interactions)** *Adsorbed molecules interact with each other neither laterally (along the surface) nor vertically (normally to the surface).*

**L3 (Surface homogeneity)** *All sites are equivalent.*

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<sup>2</sup> The difference between starting directly from statistical mechanics and starting from the dynamic system is, *mutatis mutandis*, similar to the difference between Carathéodory and Gibbs thermodynamics: the former is based on a less restrictive set of primitive concepts, derives the notions of temperature and entropy, but does not contain elements to judge about its validity; in the latter, assuming temperature and entropy as primitive concepts, attention is focused on the system providing for it a more accurate physico-chemical description and criteria for its validity. In Carathéodory thermodynamics all transformations are non-singular, while in Gibbs thermodynamics singular transformations are shown to determine the limits of system stability [17].

**L4 (Adsorption kinetics)** *The adsorption rate  $R_+$  is proportional to the amount  $N_o$  of empty sites multiplied by the gas-phase flux  $\Phi$  impinging onto the surface:*

$$R_+ = \sigma_+ \Phi N_o \quad (1)$$

$\sigma_+$  being the cross section of the process.

**L5 (Desorption kinetics)** *The desorption rate  $R_-$  is proportional to the amount  $N_*$  of occupied sites:*

$$R_- = N_* / \tau_- \quad (2)$$

$\tau_-$  being the lifetime of the process.

**L6 (Gas ideality)** *The gas phase is ideal and described by the kinetic theory of gases (with covolume).*

**L7 (Structureless adsorbate)** *The internal degrees of freedom of the molecule are not modified by adsorption, and adsorption is insensitive to them.*

**L8 (Absence of surface reconstruction)** *The total amount of sites  $N_m$  remains unchanged during AD-sorption:*

$$N_m := N_o + N_* = \text{constant}; \quad (3)$$

*what may change is only their relative occupation.*

The quantities  $N_o$ ,  $N_*$ ,  $N_m$ ,  $R_+$  and  $R_-$  are all referred to the unit area.

### 2.1.2. The parameters of the theory

Axiom L6 determines the dependence of  $\Phi$  on gas pressure  $p$  and temperature  $T$ :

$$\Phi = p / \sqrt{2\pi m k_b T} \quad (4)$$

where  $k_b$  is the Boltzmann constant and  $m$  is the molecular mass.

The quantities  $p$ ,  $\sigma_+$  and  $\tau_-$  are free parameters of the theory;  $p$  is a property of the gas alone, while  $\sigma_+$  and  $\tau_-$  are specified by the interaction between adsorbent and adsorbate.

The cross-section  $\sigma_+$  may be considered as the product of the geometric cross-section  $\sigma_{\text{geo}}$  times the sticking probability  $s$ ,

$$\sigma_+ = s\sigma_{\text{geo}} \quad (5)$$

In turn,  $\sigma_{\text{geo}}$  may be assumed to be a combination of the geometric cross-sections of the empty site,  $\sigma_{\circ}$ , and of the gas-phase molecule,  $\sigma_{\text{mol}}$ :

$$\sigma_{\text{geo}} = \left( \sigma_{\circ}^n + \sigma_{\text{mol}}^n \right)^{1/n} \quad (6)$$

with tentatively  $n = 2$  (this is the unique point where gas covolume plays a role in Langmuir's theory). Extended compilations of molecular cross sections  $\sigma_{\text{mol}}$  are available, based either on bulk (liquid or gas) phase properties of the adsorbate [19] or on molecular dynamics simulations [20].

The sticking coefficient  $s$  is related to the detailed mechanism through which a molecule in translational motion imparts its kinetic energy to the adsorbent, eventually allowing its capture in a bound state. Very little can be said in general on  $s$ ;  $\mathcal{L}$  assumes the constancy of  $s$  with  $N_{\circ}$  and  $N_{\bullet}$ .

For activated processes the desorption lifetime  $\tau_-$  can be expressed as

$$\tau_- = \tau_{0-} \exp[E/k_B T] \quad (7)$$

where  $\tau_{0-}$  is a suitable pre-exponential factor and  $E$  is the activation energy of this process<sup>3</sup>. For physisorption  $E$  may be assumed to coincide with the adsorption energy  $q$ .

### 2.1.3. Equilibrium and kinetic properties

Defining the surface coverage  $\Theta$ ,

$$\Theta := N_{\bullet} / (N_{\circ} + N_{\bullet}) = N_{\bullet} / N_m$$

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<sup>3</sup> The following symbols are systematically used: parentheses, '(' and ')', to denote the operation of considering together the symbols therein; brackets, '[' and ']', to specify the argument of functions (thus adopting the same convention as in MATHEMATICA); and braces '{' and '}', to denote the set therein listed or described. A single brace is used to denote different cases.

and the adsorption lifetime  $\tau_+$ ,

$$\tau_+ := 1/\sigma_+\Phi = \sqrt{2\pi mk_b T} / \sigma_+ p$$

the time derivative of  $\Theta$  is obtained combining Eqs.(1), (2) and (3) with conservation of matter:

$$\frac{d\Theta}{dt} = \frac{1}{\tau_+}(1-\Theta) - \frac{1}{\tau_-}\Theta \quad (8)$$

Since  $\tau_+$  and  $\tau_-$  are independent of  $N_\circ$  and  $N_\bullet$  (because of L 2), they can be considered constant in Eq. (8). Equation (8) can thus be solved for  $\Theta$  giving

$$\Theta[t] = \bar{\Theta} + (\Theta_0 - \bar{\Theta})\exp[-t/\tau_L] \quad (9)$$

where:  $\tau_L$  is the harmonic sum of  $\tau_+$  and  $\tau_-$ ,

$$\tau_L^{-1} := \tau_+^{-1} + \tau_-^{-1}$$

$\Theta_0$  is the initial coverage,  $\Theta_0 = \Theta[0]$ ; and  $\bar{\Theta}$  is the equilibrium coverage,

$$\bar{\Theta} = \frac{1}{\tau_+} \left( \frac{1}{\tau_+} + \frac{1}{\tau_-} \right)^{-1} = \frac{\sigma_+\Phi}{\sigma_+\Phi + 1/\tau_-} \quad (10)$$

Equation (9) specifies that the decay of the coverage  $\Theta$ , from its initial value  $\Theta_0$  to the equilibrium one  $\bar{\Theta}$ , is exponential in character.

Therefore,  $\mathcal{L}$  gives explicitly, through Eqs. (9) and (10), the amount  $N$  of adsorbed molecules ( $N = N_\bullet$ , because of L 1) vs. time as well as vs. the environmental quantities (like pressure  $p$  and temperature  $T$ ) which specify  $\Phi$  and  $\tau_-$ .

In a pictorial view, the Langmuir theory of AD-sorption  $\mathcal{L}$  can be summarized by the reactions ( $I_+$ ) and ( $I_-$ ) sketched in Figure 1. The rate equation (8) can be deduced from the scheme of Figure 1 by direct application of the mass-action law:

$$\frac{dN_\bullet}{dt} = AN_\circ - BN_\bullet \quad (11)$$

$$\frac{dN_{\circ}}{dt} = -AN_{\circ} + BN_{\bullet} \quad (12)$$

which yield exactly  $\mathcal{L}$  provided that<sup>4</sup>

$$A = \sigma_{+}\Phi \quad (13)$$

$$B = \tau_{-}^{-1} \quad (14)$$

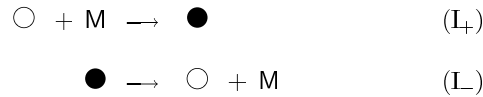


Fig. 1. The reactions at the basis of the Langmuir theory.

Although simple and elegant,  $\mathcal{L}$  does however suffer from the most serious difficulty: the kinetics and equilibria of really few systems can be described by Eqs. (9) and (10), respectively. This difficulty would be ruinous were it not for the fact that it is possible to account for most of the experimental behaviours simply relaxing one or the other of the hypotheses L 1 - L 8.

## 2.2. Relaxing the assumptions of the Langmuir theory

In a way, the set of axioms L 1, ..., L 8 forms a kind of basic axiomatic kit for the description of AD-sorption; with the substitution of one or more of them, one can create another axiomatic scheme able to account for other phenomena. The several descriptions generated continuing this game cover almost all the observed phenomena. It is worth mentioning that Langmuir himself was aware of this possibility and in the founding paper he considered

<sup>4</sup> The presence of a flux in the rate equation may seem inconsistent with the mass-action law. However, the gas law specifies the concentration as  $c = p/k_B T$  so that the factor  $A$  may be expressed in terms of concentration rather than flux,

$$A = \sigma_{+}\Phi = c\sigma_{+}k_B T / \sqrt{2\pi mk_B T}$$

Similarly, the surface concentrations  $N_{\circ}$  and  $N_{\bullet}$  may be transformed in volume concentrations  $n_{\circ}$  and  $n_{\bullet}$  dividing them by the width  $\Delta x$  of the surface region:  $n_{\circ} = N_{\circ} / \Delta x$  and  $n_{\bullet} = N_{\bullet} / \Delta x$ .

also the cases of: sites which can host more than one adsorbed molecule, adsorbed films more than one-molecule in thickness, and heterogeneous surfaces [18]. Without pretending to be exhaustive, in the following I shall briefly discuss how it is possible to account for many AD-sorption phenomena by minor changes in the axiomatic framework of  $\mathcal{L}$ .

### 2.2.1. Beyond the one-molecule/one-site approximation

The one-molecule/one-site approximation is a truly ideal case which applies to localized AD-sorption of molecules on a distribution of sites separated by a larger distance than the molecular diameter. This implies that the approximation can safely be applied to the physisorption or chemisorption of small molecules (like noble gases or  $N_2$  for physisorption, or NO for chemisorption) on relatively flat surfaces dominated by faces with low Miller indices (*i.e.* where surface atoms have high coordination number). The surfaces of larger practical interest, for instance in catalysis, are however highly heterogeneous with a strongly irregular distribution of adsorption sites.

**Allowing for multisite occupation by a single molecule.** Consider chemisorption of a molecule held at the surface by one bond alone but sufficiently large to mask a few surface sites from the outer atmosphere. In this case, the adsorption of one molecule while fills one site 'deactivates'  $N_s \sigma_{mol} - 1$  other sites. The situation is much more complicated when the molecule is held at the surface by two or more bonds. The complex statistico-mechanical counting of the available sites while the process proceeds is considered in Ref. [21].

The opposite consideration applies to physisorption. In this case, where chemical specificity is modest, the adsorption of large molecules on a strongly irregular distribution of adsorption sites may be taken into account by assuming that the adsorption of a molecule with cross section  $\sigma_{mol}$  while covering  $(N_s + N_a) \sigma_{mol}$  adsorption sites fills  $N_s \sigma_{mol}$  of them. This is equivalent to saying that adsorbed molecules can partially overlap eventually leading to multilayer adsorption.

**Allowing for multiple occupation of single sites.** Describing multilayer AD-sorption requires that axioms L 1 and L 2 are given up. However, the assumptions, that each newly adsorbed molecule is the site for adsorption of another molecule (thus contradicting L 1 and L 2) and that this process continues to be described by L 3, ..., L 8, provide a scheme for the multilayer extension of the Langmuir theory.



A somewhat different approach, in which multilayer adsorption is allowed, though AD-sorption is still described by the Langmuir theory for each layer, is at the basis of the Brunauer-Emmett-Teller theory of localized multilayer AD-sorption [22]. This theory describes equilibrium AD-sorption with an isotherm (the celebrated BET isotherm, from the initials of its proponents) which has become a standard for the determination of surface areas of real adsorbents.

### 2.2.2. Allowing for lateral interactions

As far as multilayer AD-sorption is allowed, L 2 is necessarily violated. The intermolecular interactions considered by the BET theory, however, occur 'vertically' between neighbouring molecules in the same adsorption pile.

It is possible to violate L 2 preserving the validity of L 1 (so that these axioms are independent), in which case one speaks of 'lateral' interactions. Lateral interactions in the monolayer regime may be accounted by assuming that desorption is an activated process described by Eq. (7, and admitting that  $E$  depends on  $\Theta$ ,  $E = E[\Theta]$ .

In particular, the case of a linear dependence,

$$E[\Theta] = E_0 + \omega\Theta \quad (15)$$

(with  $E_0 = E[0]$  and  $\omega$  is a quantity related to the strength of lateral interactions), has been considered. The effect of this correction depends on the sign of  $\omega$ : For  $\omega > 0$  Eq. (15) reduces an equilibrium isotherm (the Frumkin-Fowler-Guggenheim isotherm [23]) which displays the possibility of a two-dimensional phase transition at low temperature [24]. For  $\omega < 0$  one reproduces the Temkin isotherm under equilibrium conditions or the Elovich equation under nonequilibrium [25].

The Elovich equation [26] describes a time-logarithmic behaviour equation

$$N[t] - N[0] = r_0 t_m \ln[1 + t/t_m] \quad (16)$$

which is often found to describe adsorption (for  $r_0 > 0$ ) or, though less frequently, desorption (for  $r_0 < 0$ ) phenomena. In Eq. (16)  $r_0$  denotes the initial AD-sorption rate while  $t_m$  denotes the characteristic time over which the logarithmic behaviour prevails over the linear one:

$$N[t] - N[0] \cong \begin{cases} r_0 t & \text{for } t \ll t_m \\ (r_0 t_m / \gamma)(t/t_m)^\gamma & \text{for } t \gg t_m \end{cases}$$

The Elovich equation applies to so many situations (AD-sorption kinetics from solids, oxidation of metals, etc.) to have attracted numerous investigations. The explanation which attributes the time-logarithm law in AD-sorption phenomena to an activation energy increasing linearly with surface coverage because of lateral interactions [25] is not unique: Fixed energy heterogeneity [27-30] and surface reconstruction [31,32] can almost equivalently be advocated (see Section 2.2.3 and 3.1, respectively).

Another equation which is often found to describe AD-sorption phenomena is the time-power law,

$$N[t] - N[0] = \frac{r_0 t}{\gamma} \left( \left( 1 + \frac{t}{t_m} \right)^\gamma - 1 \right) \quad (17)$$

where  $r_0$  and  $t_m$  maintain the same meaning as in Eq. (16)

$$N[t] - N[0] \cong \begin{cases} r_0 t & \text{for } t \ll t_m \\ (r_0 t_m / \gamma) (t / t_m)^\gamma & \text{for } t \gg t_m \end{cases}$$

while  $\gamma$  is a suitable parameter (with  $0 < \gamma < 1$ ).

Though defined only for  $\gamma > 0$ , the limit of Eq. (17) for  $\gamma \rightarrow 0$  is just the Elovich equation, Eq. (16)<sup>5</sup> following Landsberg [32], one may thus take Eq. (17) with  $\gamma \geq 0$  as a general expression accounting for the time-logarithm and time-power laws.

### 2.2.3. Allowing for surface heterogeneity

Rather than in terms of desorption lifetime, it is convenient to express the equilibrium isotherm in terms of activation energy for desorption,  $\bar{\Theta} = \bar{\Theta}[p, E]$ . Most surfaces are energetically heterogeneous. In the Langmuir scheme, surface heterogeneity is simply taken into account assuming, instead of L 3, that the surface is characterized by a distribution  $\phi[E]$  of activation energy,

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<sup>5</sup> To show that, first write

$$(1 + t/t_m)^\gamma = e^{\ln[(1+t/t_m)^\gamma]} = e^{\gamma \ln[1+t/t_m]}$$

and then expand the exponential in Maclaurin series

where  $\phi[E]dE$  is the fraction of sites with activation energy between  $E$  and  $E + dE$ ;  $\phi[E]$  satisfies the conditions of non-negativity,

$$\forall E(\phi[E] \geq 0) \quad (18)$$

and of normalization,

$$\int_0^{\infty} \phi[E]dE = 1 \quad (19)$$

The theory of AD-sorption on heterogeneous surfaces has mainly been applied to physisorption; since in physisorption  $E$  coincides with the adsorption energy  $q$ , the formulas in the following will be given in terms of  $q$ . Moreover, most physisorption kinetics are very fast, so that for them only the equilibrium properties are experimentally accessible. Finding which equilibrium AD-sorption properties are controlled by a certain energy distribution function  $\phi[q]$ , is the matter of the theory of AD-sorption on heterogeneous surfaces. In more detail, the objectives of this theory, in the case of equilibrium AD-sorption, are to demonstrate that:

- (i) the experimental AD-sorption isotherms  $\theta(p)$  can actually be expressed as

$$\theta(p) = \int_0^{+\infty} \Theta[p, q] \phi[q] dq \quad (20)$$

with  $\phi[q]$  obeying the non-negativity and normalization conditions; and

- (ii) the distribution function which according to Eq.(20) accounts for a certain experimental isotherm is the real adsorption energy distribution of the adsorbent.

An enormous amount of work has been devoted to this subject. I simply mention that the isotherms typically observed for common adsorbents and adsorbates (the Freundlich, Dubinin-Radushkevich, and Temkin isotherms; their blends; and the Tóth equation) can be accounted for in the above terms. For details on problem (i) see Refs. [33-37,42,43]; problem (ii) is considered in Refs. [35,37]. The frequent observation of the Freundlich, Dubinin-Radushkevich, and Temkin isotherms is explained in terms of AD-sorption on equilibrium surfaces. The key role of equilibrium surfaces in determining the AD-sorption behaviour was first first suggested in Ref. [38] and is now largely accepted [39-41,35,42,43].

As first observed by Jaroniec and Madey [34], most of what holds for equilibrium can be extended to kinetics. In the frame of the theory of AD-sorption on heterogeneous surfaces, kinetics (16) and (17) are accounted for in terms of uniform or exponentially decreasing distribution functions, respectively [44,45].

#### 2.2.4. Allowing for different AD-sorption kinetics

To account for many experimental situations, the sticking coefficient  $s$  must be so chosen to depend, even strongly, on the coverage  $\Theta$ ,  $s = s[\Theta]$ . This occurrence may be phenomenologically incorporated in Langmuir's theory allowing  $\sigma_+$  to vary with  $\Theta$  as predicted by Eq. (5) with  $s = s[\Theta]$ , and preserving the validity of Eq. (8) with  $\tau_+ = \tau_+[\Theta]$ .

If the AD-sorption reactions involve more than one site per molecule, one must first consider how many sites, and in which configurations, participate in the reactions. The number of such configurations must then be calculated (thus generating in general a complex problem of lattice statistics) and substituted for  $N_{\circ}$  and  $N_{\bullet}$  in Eq. (1) and (2), respectively.

Reaction orders  $\kappa$  different from 2 (in adsorption) or 1 (in desorption) can formally be allowed for by the substitution of  $N_{\circ}^{\kappa-1}$  for  $N_{\circ}$  in Eq. (1) or of  $N_{\bullet}^{\kappa}$  for  $N_{\bullet}$  in Eq. (2).

#### 2.2.5. Relaxing the hypothesis of gas ideality

Allowing for gas-phase non-ideality has occasionally been done in the past. The most famous example is the procedure adopted by Brunauer, Emmett and Teller in deriving the BET equation: First they assumed the gas as ideal and derived an expression for the average coverage of the surface; then they observed that the expression so derived diverges at a certain pressure  $p_{\infty}$ ; and eventually they allowed for the non-ideality of the vapor assuming that the divergence occurs because of vapor condensation at the surface (putting  $p_{\infty} = p_{\text{sat}}$ , the vapor saturation pressure) [22].

Other examples are: (i) the kinetic derivation of Jovanovic isotherm by Jovanovic himself [46], in a theoretical scheme in which the collisions of desorbing molecules against gas-phase molecules are considered; and (ii) the statistico-mechanical derivation of the same isotherm by Cerofolini [47], in which the non-uniformity of the gas close to the surface and the role of the sticking coefficient in determining the surface potential are taken into account.

The most flexible way to take into account gas non-ideality is however provided by Ward's statistical rate theory [10-12], already discussed.

### 2.2.6. Allowing for internal degrees of freedom

The assumption that the adsorbed molecule does not change its internal state after adsorption is certainly a crude approximation. The basic mechanisms of catalysis (Langmuir-Hinshelwood and Eley-Rideal) are just based on the observation that, after adsorption, the adsorbed molecule attains a particularly reactive state.

Ignoring this aspect, it seems a plausible approximation that in most situations (and especially in physisorption) the parameters which describe the molecule in gas or liquid phase do not change after adsorption. In particular this seems true for a geometric parameter like the geometric cross section  $\sigma_{\text{mol}}$ .

A way to estimate the fractal dimension of a surface is to determine the surface areas of the adsorbent using a homogeneous family of molecules (*e.g.*, alkanes of different length  $n$  and hence cross section  $\sigma_{\text{mol},n}$ ) and considering the limit for  $\sigma_{\text{mol},n} \rightarrow 0$  [48]. The study of this limit for several adsorbents led Avnir, Farin and Pfeifer to assess the fractal nature of a few of them [49]. Clearly enough, this procedure is correct only if  $\sigma_{\text{mol},n}$  does not change after adsorption (or at least if  $\sigma_{\text{mol},n}$  is modified by the same factor for all  $n$ ). Actually, the discussion of Ref. [50] shows that the validity of this assumption is not guaranteed.

### 2.2.7. Allowing for surface reconstruction

In many instances adsorption, and especially chemisorption, results in adsorbate-induced reconstruction. Accounting for surface reconstruction in the spirit of this work (*i.e.*, by replacing L 8 with an axiom sufficiently realistic to describe physical situations but simple enough to allow mathematics to be handled) has been demonstrated to be a difficult task.

Two major theoretical schemes have been proposed: the first method was developed (mainly by Landsberg) to account for kinetics, while the other was developed (mainly by Cerofolini) to account for equilibrium. The kinetic approach was applied to explain the time-logarithm [31] and time-power law [32]; the equilibrium approach was applied to describe AD-sorption-induced surface reconstruction [51] and protein folding-unfolding [52].

In principle both these approaches could be used to formulate a general theory of equilibrium and kinetics of AD-sorption phenomena on reconstructing surfaces. The equilibrium approach, equipped with the statistical rate theory,

should indeed provide an adequate description of rate processes too. In line with the spirit of this work, the equilibrium approach is not followed here because it may be applied only to situations which admit equilibrium, while I am also interested in determining which situations do really admit equilibrium.

In the following I shall thus limit my attention to the kinetic scheme, obtaining the AD-sorption equilibrium (if existing) as a special case of the kinetic behaviour.

### 3. A THEORY FOR AD-SORPTION ON SURFACES UNDERGOING RECONSTRUCTION

#### 3.1. The Landsberg model for adsorption kinetics on reconstructing surfaces

In an intriguing paper [31], Landsberg formulated a model to account for the Elovich equation, basing on the assumption that the surface undergoes a reconstruction while adsorption proceeds.

First of all, Landsberg ignored desorption (thus precluding to himself the possibility of establishing an equilibrium isotherm) and considered the following axioms (reformulated to be consistent with the symbols of this work):

**R 1 (Adsorption kinetics)** *Adsorption occurs via the collision of impinging gas-phase molecules on empty surface sites.*

**R 2 (Reconstruction rate)** *Adsorption is responsible for surface reconstruction via generation of new empty sites at a rate proportional to the chemisorption rate.*

**R 3 (Self-similar reconstruction)** *Each newly exposed zone has the same topography as the surface from which it was generated.*

**R 4 (Progressive coverage)** *The process proceeds with a progressive reduction of the empty sites.*

Concretely, Landsberg formalized R 1, R 2, R 3 and R 4 as follows:

$$dN_{\bullet} / dt = \sigma_{+} \Phi N_{\circ} \quad (21)$$

$$dN_{\circ} / dt = \beta dN_{\bullet} / dt \quad (22)$$

$$\beta = bN_{\bullet} \quad (23)$$

$$b < 0 \quad (24)$$

where  $\beta$  represents the net empty sites lost per adsorbed molecule (resulting from the difference between the sites filled after adsorption and the empty sites

correspondingly generated) while  $b$  is the net area occupied per adsorbed molecule.

Combining Eqs. (21), (22) and (23) one gets

$$dN_0 / dt = b\sigma_+ \Phi N_0^2$$

that can be solved by separation of variables:

$$N_0[0]/N_0[t] = 1 - b\sigma_+ \Phi N_0[0]t \quad (25)$$

where  $N_0[0]$  is the amount per unit area of empty sites at  $t = 0$ . Inserting Eq. (25) into Eq. (21), one gets a differential equation that can in turn be solved by separation of variables:

$$N_0[t] = -\frac{1}{b} \ln[1 - b\sigma_+ \Phi N_0[0]t] \quad (26)$$

Assumption (24) is explicitly taken into account substituting  $-|b|$  for  $b$  in Eq. (26):

$$N_0[t] = \frac{1}{|b|} \ln[1 + |b|\sigma_+ \Phi N_0[0]t] \quad (27)$$

The comparison of (16) with (27) shows that they coincide provided that

$$r_0 = \sigma_+ \Phi N_0[0]$$

$$t_m = \frac{1}{|b|\sigma_+ \Phi N_0[0]}$$

thus furnishing the empirical parameters of the Elovich equation with a microscopic structural meaning. This result was the starting point for further developments:

- In a second paper Landsberg showed that minor changes in the axioms (allowing for kinetics of order different from 2) are able to account for the general kinetics, Eq. (17) [32]
- The fact that condition (24) is never used in the derivation of of Eq. (26) led Cerofolini to consider the hypothesis that this equation holds true for  $b > 0$  too. This case is qualitatively different from that considered by

Landsberg because while Eq. (27) diverges smoothly only for  $t \rightarrow +\infty$ , Eq. (26) diverges for  $t \rightarrow t_m$ . (thus providing an example of explosive dynamic system).

In spite of these interesting features, the Landsberg model has often been regarded suspiciously because of its disturbing features:

1. for no value of its free parameter  $b$  the Landsberg model is reduced to the Langmuir theory (even with  $\tau_- = +\infty$ );
2. the kinetic equation (22) links rate (of reconstruction) to rate (of adsorption) rather than rate to concentration, as it would be expected from an application of the mass-action law; and
3. the assumption R 3, specified quantitatively by Eq. (23), appeared (when formulated, in 1952) an *ad hoc* hypothesis difficult to sustain on physical bases.

The birth of the theory of fractals has made up the last difficulty: the fact that, while adsorption proceeds, the surface undergoes a reconstruction depending on the pre-existing density of sites may be interpreted in terms of a kind of self-similar growth.

In view of the ability of the Landsberg model to account for the Elovich equation in terms of self-similar reconstruction, it would be interesting to incorporate the model in a theory  $\mathfrak{S}$  such that:

1.  $\mathfrak{S}$  is constructed on the mass-action law;
2.  $\mathfrak{S}$  reduces to the Langmuir theory in the absence of reconstruction; and
3.  $\mathfrak{S}$  reproduces the Landsberg model in the absence of desorption and for certain reconstruction.

This incorporation would produce a genuine equilibrium and kinetic theory of *AD-sorption on surfaces undergoing adsorption-induced reconstruction*.

### 3.2. The dynamic description of surfaces undergoing AD-sorption-induced reconstruction

Before trying to formulate axiomatically the theory, I observe that the constancy of the total amount of sites  $N_o + N_s$  in the Langmuir theory arises from the fact that the total amount of sites on the l.h.s. of the complexive reaction in Figure 1 coincides with that on the r.h.s. Dynamic systems with surface reconstruction, once sketched as reactions involving empty and filled sites, in general do not satisfy the above condition.



The dynamic system adopted in this work for describing AD-sorption on reconstructing surfaces is sketched in Figure 2, where the free parameters of the theory,  $\alpha_+$  and  $\alpha_-$ , may be functions of  $N_o$ ,  $N_+$  or  $T$ , but not of quantities like the pressure  $p$  of the gas [53].

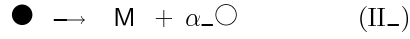
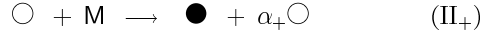


Fig. 2. The reactions at the basis of AD-sorption models with self-reconstruction.

The rate equations for the dynamic system  $\{(\text{II}_+), (\text{II}_-)\}$  are

$$\frac{dN_+}{dt} = AN_+ - BN_+ \quad (28)$$

$$\frac{dN_o}{dt} = (\alpha_+ - 1)AN_o - \alpha_- BN_+ \quad (29)$$

where  $A$  and  $B$  have the same meaning as in Eqs. (11) and (12), thus taking the values specified by Eqs. (13) and (14), respectively.

### 3.3. When the parameters allow equilibrium

For any dynamic system the equilibrium states play a special role. At equilibrium  $dN_+/dt = 0$  and  $dN_o/dt = 0$ , so that an equilibrium state exists if the parameters  $A$ ,  $B$ ,  $\alpha_+$  and  $\alpha_-$  are such that the system

$$\begin{cases} 0 = AN_+ - BN_+ \\ 0 = (\alpha_+ - 1)AN_o + \alpha_- BN_+ \end{cases} \quad (30)$$

admits a non-trivial solution  $(\bar{N}_o, \bar{N}_+)$  at least, in addition to the trivial solution  $(0,0)$  which satisfies condition (30) for all values of the parameters.

Observe now that the total number of sites in an AD-sorption cycle  $(\text{II}_+)$  and  $(\text{II}_-)$  varies by an amount  $\alpha_+ + \alpha_- - 1$ , so that the surface undergoes a *reversible* reconstruction when

$$\alpha_+ + \alpha_- = 1 \quad (31)$$

while the reconstruction is *irreversible* when  $\alpha_+ + \alpha_- \neq 1$ .

For the search of the equilibrium states it is convenient to distinguish the singular case, in which  $\alpha_+ - 1$  is identically null (at least in a non-meager compact set of the  $\{N_\circ, N_\bullet\}$  plane), from the general case, in which  $\alpha_+ - 1 \neq 0$ .

### 3.3.1. Equilibrium in the singular case

In the singular case system (30) is reduced to

$$\begin{cases} 0 = AN_\circ - BN_\bullet \\ 0 = \alpha_- BN_\bullet \end{cases}$$

Excepting the trivial solution, the above equations are mutually compatible only for  $\alpha_-$  identically null,  $\alpha_- = 0$ , or for  $\alpha_-$  any function  $\alpha_-[N_\circ, N_\bullet]$  such that  $\alpha_-[N_\circ(A/B)N_\bullet] = 0$ .

### 3.3.2. Equilibrium in the general case

Consider now the general case, with  $\alpha_+ - 1 \neq 0$ . Let  $\varepsilon$  be the net number of empty sites generated per adsorption event,

$$\varepsilon = \alpha_+ - 1$$

( $\varepsilon$  is a kind of *reconstruction degree* of the surface), and  $\delta$  be the net number of empty sites produced in an AD-sorption cycle per newly formed site,

$$\delta = \frac{\alpha_+ + \alpha_- - 1}{\alpha_+ - 1} = 1 + \frac{\alpha_-}{\alpha_+ - 1}$$

( $\delta$  is a kind of *irreversibility degree* of the process). Taking  $\varepsilon$  and  $\delta$  as independent variables, Eqs. (28) and (29) become

$$\frac{dN_\bullet}{dt} = AN_\circ - BN_\bullet \quad (28)$$

$$\frac{dN_{\circ}}{dt} = \varepsilon(AN_{\circ} - (1-\delta)BN_{\bullet}) \quad (29)$$

which reduce to Eqs. (11) and (12), respectively, for  $\varepsilon = -1$  and  $\delta = 0$ .

For dynamic system {(32),(33)} the equilibrium condition, Eq. (30), reads

$$\begin{cases} 0 = AN_{\circ} - BN_{\bullet} \\ 0 = \varepsilon(AN_{\circ} - (1-\delta)BN_{\bullet}) \end{cases} \quad (34)$$

with  $\varepsilon = \varepsilon[N_{\circ}, N_{\bullet}]$  and  $\delta = \delta[N_{\circ}, N_{\bullet}]$ . Conditions (34) are manifestly compatible when  $\delta = \delta[N_{\circ}, N_{\bullet}]$  is identically null,

$$\forall N_{\circ}, N_{\bullet} (\delta[N_{\circ}, N_{\bullet}] = 0) \quad (35)$$

Equilibrium is however allowed even when condition (35) is violated provided that:

- irrespective of  $\varepsilon[N_{\circ}, N_{\bullet}]$ , the roots of  $\delta[N_{\circ}, N_{\bullet}] = 0$  satisfy also the condition  $AN_{\circ} = BN_{\bullet}$ , in which case the equilibrium state is obtained solving the equation  $\delta[N_{\circ}, (A/B)N_{\bullet}] = 0$ ; or
- irrespective of  $\delta[N_{\circ}, N_{\bullet}]$ , the roots of  $\varepsilon[N_{\circ}, N_{\bullet}] = 0$  satisfy also the condition  $AN_{\circ} = BN_{\bullet}$ , in which case the equilibrium state is obtained solving the equation  $\varepsilon[N_{\circ}, (A/B)N_{\bullet}] = 0$ .

Unless the functions  $\varepsilon[N_{\circ}, N_{\bullet}]$  and  $\delta[N_{\circ}, N_{\bullet}]$  are specified, it is impossible to state anything about their zeros.

For a large class of functions  $\varepsilon[N_{\circ}, N_{\bullet}]$  of physical interest the roots of the equation  $\varepsilon[N_{\circ}, N_{\bullet}] = 0$  are either trivial (e.g.,  $\varepsilon[N_{\circ}, N_{\bullet}] = \gamma'^2 N_{\circ} + \gamma''^2 N_{\bullet}$ , with  $\gamma'$  and  $\gamma''$  arbitrary constants) or even unphysical (e.g.,  $\varepsilon[N_{\circ}, N_{\bullet}] = \gamma'^2$ ). For these functions equilibrium is possible either for  $\delta[N_{\circ}, N_{\bullet}]$  identically null (that implies reversible reconstruction) or for states along which the system undergoes reversible reconstruction.

### 3.4. Specializing the description to surfaces undergoing reversible reconstruction

The theory described by Eqs. (28) and (29) with  $\alpha_+$  and  $\alpha_-$  given functions of  $N_0$  and  $N_1$ , however stratifying the reversibility condition, Eq. (42), will be denoted with  $\mathfrak{R}$ . In the following the attention will be limited to  $\mathfrak{R}$ .

Even the dynamics of surfaces undergoing AD-sorption-induced reconstruction is better considered analyzing the singular case separately from the general case.

#### 3.4.1. Dynamics in the singular case

In the singular case the dynamics of AD-sorption on surfaces undergoing reversible reconstruction is described by putting  $\alpha_+ - 1 = 0$  and  $\alpha_- = 0$  in Eqs. (28) and (29):

$$dN_1 / dt = AN_0 - BN_1 \quad (36)$$

$$dN_0 / dt = 0 \quad (37)$$

These equations are integrated immediately: Eq. (36) gives

$$N_1[t] = N_1[0] \quad (38)$$

the initial amount of empty sites; the insertion of this value into Eq. (36) gives a differential equation whose solution is straightforward:

$$N_1[t] = \bar{N}_1 + (N_1[0] - \bar{N}_1) \exp(-Bt)$$

where  $\bar{N}_1$  is the equilibrium amount of filled sites:

$$\bar{N}_1 = (A/B)N_0[0]$$

#### 3.4.2. Dynamics in the general case

Even the dynamics of the general case is better described in terms of  $\varepsilon$  and  $\delta$ , for which

$$\frac{dN_1}{dt} = AN_0 - BN_1 \quad (38)$$

$$\frac{dN_{\circ}}{dt} = \varepsilon(AN_{\circ} - BN_{\bullet}) \quad (39)$$

$$\varepsilon = \varepsilon[N_{\circ}, N_{\bullet}] \quad (40)$$

where the non-null function  $\varepsilon[N_{\circ}, N_{\bullet}]$  in Eq. (40) is determined by the kind of reconstruction. The dynamics in the general case is controlled by this function. In the absence of further information, the maximum one can say is obtained dividing member-by-member Eqs. (29) and (38) thus getting

$$dN_{\circ}dN_{\bullet} = \varepsilon[N_{\circ}, N_{\bullet}] \quad (41)$$

If  $\varepsilon[N_{\circ}, N_{\bullet}]$  is a sufficiently regular function of the arguments, differential equation (41) (with the initial condition  $N_{\circ} = N_{\circ}^0$  for  $N_{\bullet} = 0$ ) admits a unique solution  $N_{\circ} = \eta[N_{\bullet}]$ . Nothing else can be said, unless  $\varepsilon[N_{\circ}, N_{\bullet}]$  is specified further.

Of course,  $\varepsilon[N_{\circ}, N_{\bullet}]$  must be chosen on physical grounds (to describe the actual surface reconstruction process), however satisfying the conditions of simplicity which allow Eq. (41) to be solved.

### 3.5. The last restriction – the surface undergoes self-similar reconstruction

The intuitive notion of self-similar reconstruction seems to be captured by the following

**Definition 1 (Self-similar reconstruction)** *The surface reconstruction is self-similar if net number of empty sites generated per adsorbed molecule,  $\varepsilon$ , is a function of the amount of empty sites only,  $\varepsilon = \varepsilon[N_{\circ}]$ .*

To which extent does this definition match the self-similarity considered in the theory of fractals is discussed in Ref. [54]

The theory  $\mathcal{S}$  of AD-sorption on surfaces undergoing self-similar reversible reconstruction is therefore characterized by the following axioms:

**ASSRR 1 (One-molecule/one-site)** *A site is filled by reaction with one and only one molecule; the extrasite space is unavailable for adsorption.*

**ASSRR 2 (Absence of intermolecular interactions)** *Adsorbed molecules interact with each other neither laterally (along the surface) nor vertically (normally to the surface).*

**ASSRR 3 (Surface homogeneity)** *All sites are equivalent.*

**ASSRR 4 (Adsorption kinetics)** *The adsorption rate is proportional to the amount  $N_0$  of empty sites multiplied by the gas-phase flux  $\Phi$  impinging onto the surface*

**ASSRR 5 (Desorption kinetics)** *The desorption rate  $R_-$  is proportional to the amount  $N_+$  of occupied sites:*

**ASSRR 6 (Gas ideality)** *The gas phase is ideal and described by the kinetic theory of gases.*

**ASSRR 7 (Structureless adsorbate)** *The internal degrees of freedom of the molecule are not modified by adsorption, and adsorption is insensitive to them.*

**ASSRR 8 (Self-similar reversible reconstruction)** *Adsorption results in the creation of  $\alpha_+$  empty sites per filled site while desorption results in the formation of  $\alpha_-$  per desorbed molecule; an AD-sorption cycle regenerates the original surface,*

$$\alpha_+ + \alpha_- = 1 \quad (42)$$

*and the creation-destruction process is self-similar,*

$$\alpha_+ - 1 = \varepsilon[N_0] \quad (43)$$

$\mathcal{S}$  is indeed constructed in the spirit of a theory with the minimum of changes with respect to the Langmuir theory because  $\forall n(n=1, \dots, 7) \Rightarrow \text{ASSRR } n = \text{L } n$ , the unique different axiom being the last one (ASSRR 8  $\neq$  L 8). The unique free parameter added by  $\mathcal{S}$  to the Langmuir theory is the function  $\varepsilon[N_0]$ . The basic equations which describe the considered dynamic system  $\{(II_-), (II_+)\}$  are given by Eqs. (38) and (39) with  $\alpha_+ - 1$  specified by Eq. (43):

$$\frac{dN_+}{dt} = AN_0 - BN_+ \quad (44)$$

$$\frac{dN_{\circ}}{dt} = \varepsilon[N_{\circ}](AN_{\circ} - BN_{\bullet}) \quad (45)$$

The goal of  $\mathcal{S}$  is to demonstrate that situations of large practical and conceptual interest, not allowed for in Langmuir theory, may instead be reproduced by simple specifications of  $\varepsilon[N_{\circ}]$  in Eq. (43), thus showing that the axiomatic system  $\{\text{ASSRR } 1, \dots, \text{ASSRR } 8\}$  provides the basis for a genuine extension of the Langmuir theory to self-reconstructing surfaces.

Before developing the mathematical apparatus of the theory to deal with particular cases, I shall consider a property of  $\mathcal{S}$  that holds true quite irrespective of the function  $\varepsilon[N_{\circ}]$ : The time variation of the total amount of sites is obtained summing Eqs.(38) and (39) side by side,

$$\frac{d}{dt}(N_{\circ} + N_{\bullet}) = (1 + \varepsilon[N_{\circ}])(AN_{\circ} - BN_{\bullet}) \quad (46)$$

Therefore, the total number of sites remains unchanged with time only at equilibrium (when  $AN_{\circ} - BN_{\bullet} = 0$ ) or even in non-equilibrium conditions when

$$\varepsilon[N_{\circ}] = -1 \quad (47)$$

*i. e.*, when  $\mathcal{S}$  is reduced to the Langmuir theory: the constancy with time of the total amount of sites  $N_{\circ} + N_{\bullet}$  is a peculiar property of  $\mathcal{L}$  alone.

### 3.6. The mathematical apparatus

Eliminating  $AN_{\circ} - BN_{\bullet}$  between Eqs. (44) and (45) one gets the relationship

$$dN_{\circ} = \varepsilon[N_{\circ}]dN_{\bullet} \quad (48)$$

which may be solved, for  $\varepsilon[N_{\circ}] \neq 0$ , by separation of variables:

$$\int_{N_{\circ}^0}^{N_{\circ}} \frac{dN_{\circ}}{\varepsilon[N_{\circ}]} = N_{\bullet} \quad (49)$$

(with  $N_o^0$  the amount of empty sites at  $N_s = 0$ ;  $N_o^0$  must not be confused with the amount  $N_o[0]$  of empty sites at  $t = 0$ :  $N_o^0 = N_o[0]$  only when  $N_s[0] = 0$ ). If  $\varepsilon[N_s]$  does not change its sign in the integration interval, Eq. (49) can be solved for  $N_o$ , thus giving  $N_o$  as a function of  $N_s$ :

$$N_o = \eta[N_s] \quad (50)$$

Substituting  $\eta[N_s]$  for  $N_o$  in Eq. (44) gives equation

$$\frac{dN_s}{dt} = A\eta[N_s] - BN_s \quad (51)$$

which is the key equation of the theory. In fact, the equilibrium condition is immediately obtained putting  $dN_s/dt = 0$  therein,

$$\eta[N_s] - (B/A)N_s = 0 \quad (52)$$

while the kinetics are determined solving Eq. (51) by separation of variables:

$$\int_{N_s[0]}^{N_s[t]} \frac{dN_s}{\eta[N_s] - (B/A)N_s} = At \quad (53)$$

Because of their physical meaning, the solutions of Eqs. (50-53) must satisfy the condition of non-negativity

$$\forall t (N_o[t], N_s[t] \geq 0) \quad (54)$$

#### 4. APPLICATIONS TO MONOLAYER AD-SORPTION

##### 4.1. The case of constant reconstruction

The simplest situation one can consider is that of constant reconstruction:

$$\varepsilon[N_s] = a = \text{const} \quad (55)$$



This case is very special because though formally allowed by Definition 1, it is actually associated with a reconstruction which does not depend on the state of the surface.

According to the sign of  $a$ , adsorption may result in a progressive passivation of the original sites ( $a < 0$ ) or in a growth ( $a > 0$ ). Figure 3 sketches these processes.

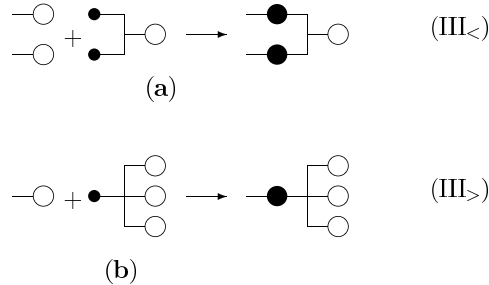


Fig. 3. Sketch of the processes leading to surface passivation ( $III_{<}$ ) or growth ( $III_{>}$ ) and the corresponding species (a) and (b), respectively. In the considered examples  $\alpha_+ = 0$  and  $\alpha_- = -1$  for (a) and  $\alpha_+ = 3$  and  $\alpha_- = -2$  for (b). Empty and full sites are denoted with large  $\circ$  and  $\bullet$  respectively; a small  $\bullet$  denotes a docking site of the molecule.

Before discussing the solutions of Eqs. (52) and (53) under condition (55), I mention that the case of constant reconstruction applies to a situation recently become of large interest – the growth of dendrimers [55]. The case of the growth of dendrimers combines multilayer growth with self-similar reversible reconstruction, in this way showing that ASSRR 1 and ASSRR 8 are independent.

#### 4.1.1. Equilibrium

Let  $a \neq 0$ . Inserting this value into Eq. (49) and integrating one has

$$N_{\circ} = N_{\circ}^0 + aN_{\bullet} \quad (56)$$

that is consistent with condition (48) even for  $a = 0$  and therefore holds true for all  $a$  (note that for  $a = -1$  it reduces to  $N_{\circ} + N_{\bullet} = N_{\circ}^0$ , giving the constancy of the number of sites).

Inserting Eq. (56) in the equilibrium condition, Eq. (52), one gets an equation that admits a unique physical solution  $\bar{N}_\bullet$  (with  $\bar{N}_\bullet > 0$ ) only for  $a < B/A$  the solution is

$$\bar{N}_\bullet = N_\circ^0 \frac{1}{B/A - a} \quad (57)$$

$$\bar{N}_\circ = N_\circ^0 \frac{B/A}{B/A - a} \quad (58)$$

Summing side by side Eqs. (57) and (58) one gets

$$\bar{N}_\circ + \bar{N}_\bullet = N_\circ^0 \left( 1 + \frac{1+a}{B/A - a} \right)$$

from which the Langmuir theory is once again reproduced ( $\bar{N}_\circ + \bar{N}_\bullet = N_\circ^0$ ) for  $a = -1$ .

#### 4.1.2. Kinetics

Inserting Eq. (56) in Eq. (53), one gets

$$\int_{N_\bullet[0]}^{N_\bullet[t]} \frac{dN_\bullet}{N_\circ^0 - (B/A - a)N_\bullet} = At$$

whose integration is elementary:

$$\ln \left[ \frac{1 - (B/A - a)N_\bullet[t]/N_\circ^0}{1 - (B/A - a)N_\bullet[0]/N_\circ^0} \right] = -A(B/A - a)t \quad (59)$$

Defining

$$\tau_a^{-1} := A(B/A - a) = B - aA$$

and remembering Eq. (57), Eq. (59) becomes

$$N_\bullet[t] = \bar{N}_\bullet + (N_\bullet[0] - \bar{N}_\bullet) \exp[-t/\tau_a] \quad (60)$$

The kinetics are therefore controlled by the sign of  $B/A - a$ : for  $B/A - a > 0$  the amount of filled sites relaxes to the equilibrium one with an exponential decrease of the initial algebraic excess; otherwise, for  $B/A - a < 0$ , the solution runs away diverging exponentially (with upward concavity) to  $+\infty$  with time constant  $|A(B/A - a)|$ . The behaviour described by (60) for the first case, exponential relaxation to equilibrium, is similar to what happens for the Langmuir isotherm; what changes is simply the time constant of the process.

#### 4.2. The case of reconstruction varying linearly with the density of available sites

In order of increasing complexity, the second case to consider is that of reconstruction varying linearly with the density of available sites,

$$\varepsilon[N_{\bullet}] = bN_{\bullet} \quad (61)$$

that is expected to be able to reproduce the Landsberg behaviour, at least in certain conditions.

Inserting Eq. (61) into Eq. (49) gives

$$N_{\bullet} = N_{\bullet}^0 \exp[bN_{\bullet}] \quad (62)$$

The insertion of Eq. (62) into Eqs. (52) and (53) gives the equilibrium and kinetic equations, respectively, for the linear case:

$$N_{\bullet}^0 \exp[bN_{\bullet}] = (B/A)N_{\bullet} \quad (63)$$

and

$$\int_{N_{\bullet}(0)}^{N_{\bullet}(t)} \frac{dN_{\bullet}}{N_{\bullet}^0 \exp[bN_{\bullet}] - (B/A)N_{\bullet}} = At \quad (64)$$

##### 4.2.1. Equilibrium

The number of solutions of the equation  $e^x = kx$  depends on the value of the parameter  $k$ ; this equation has

- one negative solution ( $\bar{x} < 0$ ) for  $k < 0$ ;
- one improper solution ( $\bar{x} = -\infty$ ) for  $k = 0$ ;
- no solution for  $0 < k < e$ ;

- two coinciding solutions ( $\bar{x} = 1$ ) for  $k = e$ ; and
- two different solutions  $x^*$  and  $x^{**}$  (with  $x^* < x^{**}$ ) for  $k > e$ .

This discussion applies to Eq. (63) writing it in the form

$$e^{bN_{\bullet}} = \frac{B/A}{bN_{\bullet}^0} bN_{\bullet} \quad (65)$$

and treating  $bN_{\bullet}$  as the variable  $x$  and  $(B/A)/bN_{\bullet}^0$  as the parameter  $k$ .

Assume first  $b < 0$ . In this case Eq. (65) admits a unique negative solution  $b\bar{N}_{\bullet}$ ; from  $b < 0$  and  $b\bar{N}_{\bullet} < 0$ , it follows that  $\bar{N}_{\bullet}$  satisfies condition (54). Putting  $B = 0$  (i. e.,  $k = 0$ ) should reproduce the same situation as considered by Landsberg, so that the improper solution  $b\bar{N}_{\bullet} = -\infty$  (i. e.,  $\bar{N}_{\bullet} = +\infty$ ), coinciding with the limit of  $N_{\bullet}[t]$  for  $t \rightarrow +\infty$  in the original Landsberg model, must be considered a kind of equilibrium value of  $N_{\bullet}[t]$ ; in this situation Eq. (62) gives  $\bar{N}_{\bullet} = 0$ .

Assume now  $b > 0$ . For  $0 < B/abN_{\bullet}^0 < e$  (corresponding to the prevalence of adsorption and reconstruction over desorption) the dynamic system does not admit any equilibrium state. Equation (65) admits, for  $B/AbN_{\bullet}^0 > e$ , two solutions  $N_{\bullet}^*$  and  $N_{\bullet}^{**}$ , that coincide for  $B/AbN_{\bullet}^0 = e$ . Recognizing which (if any) of them is the equilibrium one will follow from the discussion of kinetics.

#### 4.2.2. Kinetics

Understanding the kinetics requires the consideration of several cases.

**The case  $b < 0$ .** In this case the system admits always one equilibrium state. The kinetics are different according to the occurrence that the initial condition  $N_{\bullet}[0]$  is far from, or close to, the equilibrium value  $\bar{N}_{\bullet}$ :

- **Behaviour far from equilibrium**

The system may be far from equilibrium only in the early stages after its preparation. Its evolution will therefore be dominated either by adsorption ( $N_{\bullet}^0 e^{bN_{\bullet}} \gg (B/A)N_{\bullet}$ ) when  $N_{\bullet}[0] \ll \bar{N}_{\bullet}$ , or by desorption ( $N_{\bullet}^0 e^{bN_{\bullet}} \ll (B/A)N_{\bullet}$ ) when  $N_{\bullet}[0] \gg \bar{N}_{\bullet}$ .

If the evolution is dominated by adsorption, Eq. (64) may be approximated by

$$\int_{N_{\bullet}[0]}^{N_{\bullet}[t]} N_{\bullet}^0 \exp[-bN_{\bullet}] dN_{\bullet} \cong At$$

whose integration is straightforward:

$$N_{\bullet}[t] - N_{\bullet}[0] \cong -\frac{1}{b} \ln[1 - N_{\bullet}^0 e^{bN_{\bullet}[0]} bAt]$$

Remembering Eq. (62) one has

$$N_{\bullet}[0] = N_{\bullet}^0 \exp[bN_{\bullet}[0]]$$

so that, emphasizing that  $b$  is negative, the above kinetics become

$$N_{\bullet}[t] - N_{\bullet}[0] \cong \frac{1}{|b|} \ln[1 + |b| N_{\bullet}[0] At]$$

that reproduce the ones originally proposed by Landsberg.

If the evolution is dominated by desorption, Eq. (64) may be approximated by

$$-\int_{N_{\bullet}[0]}^{N_{\bullet}[t]} (B/A) N_{\bullet} dN_{\bullet} \cong At$$

whose integration is straightforward:

$$N_{\bullet}[t] \cong N_{\bullet}[0] e^{-Bt}$$

The kinetics in this case do therefore reduce to the ones of the Langmuir model.

- **Behaviour close to equilibrium**

The region close to equilibrium is characterized by the condition  $N_{\bullet}(t) \cong \bar{N}_{\bullet}$ ; the behaviour close to equilibrium can be studied treating the difference  $\Delta N_{\bullet} := N_{\bullet}(t) - \bar{N}_{\bullet}$  as a differential:

$$\begin{aligned}
N_{\bullet}^0 e^{bN_{\bullet}} - \frac{B}{A} N_{\bullet} &= N_{\bullet}^0 e^{b(\bar{N}_{\bullet} + \Delta N_{\bullet})} - \frac{B}{A} (\bar{N}_{\bullet} + \Delta N_{\bullet}) \\
&\approx N_{\bullet}^0 e^{b\bar{N}_{\bullet}} (1 + b\Delta N_{\bullet}) - \frac{B}{A} (\bar{N}_{\bullet} + \Delta N_{\bullet})
\end{aligned}$$

$$\frac{B}{A} (\bar{N}_{\bullet} b - 1) \Delta N_{\bullet} \quad (66)$$

because  $N_{\bullet}^0 e^{b\bar{N}_{\bullet}} - (B/A)\bar{N}_{\bullet} = 0$ . Inserting Eq. (66) in Eq. (64) and integrating one has

$$\Delta N_{\bullet}(t) = \Delta N_{\bullet}(0) \exp(-B(1 + |b| \bar{N}_{\bullet})t)$$

This equation shows that the initial algebraic excess  $\Delta N_{\bullet}[0]$  decays exponentially to 0 with lifetime  $1/B(1 + |b| \bar{N}_{\bullet})$ .

**The case  $b > 0$**

- **The system does not admit equilibrium states**

The dynamic system does not admit equilibrium states when

$$\forall N_{\bullet} (N_{\bullet}^0 \exp[bN_{\bullet}] > (B/A)N_{\bullet})$$

Since  $dN_{\bullet}/dt = N_{\bullet}^0 \exp[bN_{\bullet}] - (B/A)N_{\bullet} > 0$ ,  $N_{\bullet}[t]$  is an increasing function of  $t$  and

$$N_{\bullet} \rightarrow +\infty \Rightarrow N_{\bullet}^0 \exp[bN_{\bullet}] - (B/A)N_{\bullet} \approx N_{\bullet}^0 \exp[bN_{\bullet}]$$

Substituting  $N_{\bullet}^0 \exp[bN_{\bullet}]$  for  $N_{\bullet}^0 \exp[bN_{\bullet}] - (B/A)N_{\bullet}$  in Eq. (64) determines the asymptotic behaviour of the kinetics:

$$\int_{N_{\bullet}[0]}^{N_{\bullet}[t]} N_{\bullet}^0 \exp[-bN_{\bullet}] dN_{\bullet} \cong At$$

Its integration gives

$$N_{\bullet}[t] - N_{\bullet}[0] \cong -\frac{1}{b} \ln[1 - bN_{\bullet}[0]At]$$

Since  $b > 0$ , this equation reproduces Cerofolini's extension of Landsberg's model.

- **The system admits one equilibrium state**

For  $(B/A)bN_{\bullet}^0 > e$ , Eq. (63) admits two solutions  $N_{\bullet}^*$  and  $N_{\bullet}^{**}$  (with  $N_{\bullet}^* < N_{\bullet}^{**}$ ).

If  $N_{\bullet}^* > N_{\bullet}^{**}$ , the system evolves running away to  $+\infty$ . To demonstrate this statement observe that in this case the conditions  $N_{\bullet}^0 \exp[bN_{\bullet}] > (B/A)N_{\bullet}$  and  $dN_{\bullet}/dt > 0$  hold true at  $t = 0$  and *a fortiori* for any positive  $t$  so that the solution of Eq. (64) increases steadily with time. Thus, even though Eq. (63) admits two positive roots, neither of them is actually attained by the system; rather the asymptotic behaviour is obtained ignoring  $(B/A)N_{\bullet}$  in Eq. (64). Once again the solution of the resulting equation has the expression (67) that reproduces Cerofolini's extension of Landsberg's model.

If  $N_{\bullet}[0] < N_{\bullet}^{**}$ , the system relaxes to the equilibrium value  $N_{\bullet}^*$ . This statement is demonstrated observing that  $N_{\bullet}[t]$  decrease with  $t$  for  $N_{\bullet}^* < N_{\bullet}[0] < N_{\bullet}^{**}$  while increases with  $t$  for  $0 < N_{\bullet}[0] < N_{\bullet}^*$ , that combined together make  $N_{\bullet}^*$  the equilibrium state of the system,  $\bar{N}_{\bullet} = N_{\bullet}^*$ . For  $N_{\bullet}$  in the vicinity of  $\bar{N}_{\bullet}$ , the system evolves with time as discussed in part 4.2.2.

## 5. CONCLUSIONS

A theory has been formulated to incorporate the reconstruction phenomena occurring during adsorption and desorption within the Langmuir theory. The general formulation of the theory applies to both irreversible and reversible reconstruction. Irreversible reconstruction, however, does never admit equilibrium states and its kinetic behaviour has been ignored. The case of reversible reconstruction is more interesting and, according to the nature of reconstruction, it may admit or not non-trivial equilibrium states.

Two particular cases of self-similar equilibrium reconstruction have been considered. For constant reconstruction degree  $a$ , equilibrium is always attained when  $a < 0$ ; for  $a > 0$  it is achieved only when the gas pressure and desorption lifetime are low enough. The case of linear reconstruction is even more interesting. The behaviour of the system is controlled by the value of the parameter  $b$  linking reconstruction to density of sites: For  $b < 0$  the system admits always an equilibrium state; in this case and for negligible desorption rate the initial evolution of the system reduces to the kinetics originally predicted by Landsberg. For  $b$  small and positive the system does not admit any equilibrium state and its kinetics are described by Cerofolini's extension of Landsberg model. For  $b$  large and positive the system admits an equilibrium state, which is achieved or not in relation to the initial condition. When equilibrium is not achieved, the kinetics are once again described by Cerofolini's extension of Landsberg model.

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## CURRICULUM VITAE



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