

ON STOCHASTICS
OF ADSORPTION ON A HOMOGENEOUS SURFACE. I.
OCCUPATION OF A SINGLE SURFACE SITE

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An expression giving the probability of adsorption of a particle on a smooth homogeneous surface has been derived. The developed model takes into consideration the possibility of sliding of the particle from the occupied site to the free surface as well as the possibility of migration of the particle. Even this simple model needed certain approximations and further simplifying assumptions in order to obtain the expressions in a closed form. The influence of the activated desorption due to adsorption of the particle is stressed out; an expression that estimated this effect has been suggested.

The aim of this study is to formulate a model, as general as possible, of the stochastics of adsorption of a particle from the gaseous phase on a homogeneous surface with regard to the lucidity of the derived mathematical expressions.

This first part deals with the problem of adsorption on a single site of the surface only. The treatment is a generalized conception of the Kisliuk's model¹. The fact that a suitable choice of adjustable parameters may vary widely the characteristic dependence of the adsorption probability on the surface coverage implies that relating experimental data with a specific model of adsorption interaction should be done very cautiously. In general, two or more well fitting models can be found. In view of experimental and methodical errors, even the model best fitting the experimental data should not be regarded as the most appropriate.

Treatment of the Problem

The following treatment is based on this model: The surface exposed to the gaseous phase is monoatomic and sufficiently smooth in such a way that adsorbed particles would be distributed essentially in a random way over the entire range of coverage studied. This requires, on the one hand, an energetic homogeneity of the virgin surface and, on the other hand, such a probability of trapping of an incoming particle on a free site which would be independent of the degree of coverage of both the vicinal

sites and the entire surface. Let the mean residence time of the particles adsorbed on the virgin surface be sufficiently long in comparison with the reciprocal value of the frequency of impact of particles from the gaseous phase on the surface. Thus, desorption does not manifest itself up to a very high degree of surface coverage (this limitation will be removed in the final part of this paper, anyway).

Let us follow now the fate of particles striking the surface thus defined:

1. The particle strikes the virgin surface; during this process it either loses sufficient amount of energy to become trapped on the surface (probability p_0), or rebounds into the gaseous phase with the original or with a changed energy (probability $q_0 = 1 - p_0$). Further fate of the particle trapped on the virgin surface is of no interest to us, in this phenomenological and formal treatment, unless it perturbs the basic assumptions of this model – a random distribution. Such a particle may stay for some time at the same site, it may migrate to a vicinal site, or pass to another adsorption state. Let us assume that the reflected particles do not increase the impact frequency of gaseous particles on the surface. This assumption will be fulfilled at sufficiently low pressures when the mean free path would be long enough to let the particle fly far away from the surface so that the probability of its returning might be regarded as negligible.

2. The particle strikes an occupied site. Let us consider such a stage and such a type of adsorption that the surface is covered to a significant extent by a single layer only so that an impact of the particle onto the second adsorption layer is sufficiently improbable to be neglected; and "island" type of adsorption kinetics is excluded by the basic assumption of a random distribution. In other words, in this model the frequency of desorption from the covered surface is considerably higher than the frequency of impacts of incoming particles. The particle striking an occupied site may either remain adsorbed on its predecessor, slide to a vicinal free site, or return to the gaseous phase. The corresponding probabilities will be evaluated later on.

The treatment does not take into consideration these further possibilities: *a*) The hitting particle may displace either the struck adsorbed particle or a particle nearby and get adsorbed instead. In a certain approximation, this case can be treated formally as a reflection of the particle, with the exception of the dependence on the local surface coverage. The final part of this paper respects even this case using an intuitive dependence on the surface coverage. Removing from the surface both the hitting and the struck particle would be energetically less likely, and neglecting it does not introduce a significant error into our treatment. *b*) a particle impinging between two occupied sites may move one adsorbed particle to a vicinal free site and take its position itself. This event depends on the mobility of adsorbed particles and on the local distribution of the occupied sites. Formally, it may be approximately expressed together with the treatment of the sliding particles.

3. Contrary to the particles adsorbed on the virgin surface, further fate of the particles adsorbed on an occupied site (*i.e.* in the second layer) will be of interest to us. Such particles may essentially slide to a vicinal free site or move to a vicinal occupied site (migration over the adsorbed surface) or desorb from the surface. The particular probabilities will be again discussed later with the use of the following probability model:

The surface under consideration has N adsorption sites over an area unit; N is independent of the degree of the virgin surface coverage ϑ . Thus the area $1/N$ corresponds formally to one adsorption site surrounded by z vicinal adsorption centers. Impact of a particle is regarded as an impact on an occupied site, if its center aims at the area $1/N$ around the center of the adsorbed particle. Then the probability of striking the free surface will be $(1 - \vartheta)$ and the probability of striking an occupied site (defined in this way) will be ϑ .

Assuming a random distribution of the surface coverage, the probability that in a close proximity of a site under consideration there will be just m occupied sites in any configuration will be given by

$$P_k(m) = \binom{z}{m} \vartheta^m (1 - \vartheta)^{z-m}, \quad (1)$$

where $\binom{z}{m}$ expresses the number of particular configurations.

The probability that a particle striking an occupied site will slide to a vicinal free site depends — besides others — on the direction of the impact, on the position with respect to the center of the adsorbed particle, and on the degree of coverage of the vicinal sites. Let us sum up the first two factors to a certain average probability of sliding off an isolated adsorbed particle p_s . In this way a certain arbitrariness of an impact on a "free" or "occupied" site will be taken care of: into p_s a smaller probability of a contact with the free surface may be included, if the center of the impacting particle misses the area $1/N$, but is close enough to result in a contact between the incoming and the adsorbed particle. Let us express the probability that the sliding particle is trapped on the surface by a factor α , independent of the degree of the surface coverage.

Steric hindrance of sliding is expressed in this model by introducing a factor $\beta \leq 1$. If the two nearest positions to a vicinal occupied site (all of them neighbouring with the central position under consideration) are free, the steric hindrance of sliding is β ; if k sites next to each other (neighbouring with the central particle) are compactly occupied, the hindrance will be given by the factor $(k - 1) + \beta$, *i.e.* it is assumed that sliding can occur only at margins of this compact configuration.

Let us treat as an example the resulting probability of sliding $p'_s(3)$ for three occupied sites next to the central occupied site under consideration. 1). A fully compact configuration, where all the occupied sites lie next to each other, may be realized

in z ways and the probability of sliding to a non-occupied site is $p_s(z - 2 - \beta)/z$. 2. A semicompact configuration in which two occupied sites lie next to each other and the third one is isolated from them may be realized in $z(z - 4)$ ways and the probability of sliding is $p_s(z - 1 - 2\beta)/z$. 3. A "free" configuration in which none of the occupied sites lies next to each other be realized in $z/3 \binom{z-4}{2}$ ways and the probability of sliding is then $p_s(z - 3\beta)/z$.

Therefore, the over-all probability of sliding is

$$p'_s(3) = p_s \left[z \frac{z - 2 - \beta}{z} + z(z - 4) \frac{z - 1 - 2\beta}{z} + \frac{z(z - 4)(z - 5)}{6} \frac{z - 3\beta}{z} \right] = \\ = \frac{p_s}{3} \binom{z - 1}{2} \left[z - 3 \left(\beta + 2 \frac{1 - \beta}{z - 1} \right) \right]. \quad (2)$$

It can be shown that the probability of sliding for k occupied vicinal sites is given by

$$p'_s(k) = \frac{p_s}{k} \binom{z - 1}{k - 1} \left\{ z - k \left[\beta + \frac{(k - 1)(1 - \beta)}{z - 1} \right] \right\}. \quad (3)$$

The resulting probability that a particle striking within a certain area of the occupied site will slide to a free surface is then obtained by summing over all k and by taking into account the probability of occurrence of these configurations as given by (1) (without the configuration factor $\binom{z}{k}$ which is included in the individual configurations). The form of the probability is

$$p'_s = p_s(1 - \vartheta) Y, \quad (4)$$

where

$$Y = 1 + (1 - \beta) \vartheta. \quad (5)$$

The probability of trapping is then obtained by multiplying (4) by the factor α . Further, let us denote by α' the probability that a particle that did not slide will be trapped on an adsorbed particle. The resulting probability that a particle whose center strikes within the area of the occupied site will be trapped there is given by

$$p_0 = \alpha'(1 - p'_s) = \alpha'[1 - p_s(1 - \vartheta) Y]. \quad (6)$$

Finally, let us follow the fate of a particle trapped over an occupied site. Such a particle would vibrate around its equilibrium position. Let us regard the individual vibrations as independent, and denote the frequency of vibrations by ν . In agreement

with the previous treatment, let us consider only the fate of the particle while on the occupied surface, *i.e.* during its migration over the occupied surface. It should be noted, however, that the assumption of a different probability for adsorption on the free surface and adsorption after sliding of the particle leads in general to the requirement of the migration over the free surface in order to preserve the requirement of a random distribution. Let ${}^i p_s f$ be the probability of sliding to the free surface between two vibrations directed away from the surface in the i -th migration shift; the probability of migration to a vicinal adsorbed particle is ${}^i p_m(1 - f)$; the probability of desorption is ${}^i p_d$, and the probability that the particle remains on the surface is ${}^i p_0$ (this includes the probability that the sliding particle returns to the adsorbed particle). Evidently,

$${}^i p_s f + {}^i p_m(1 - f) + {}^i p_d + {}^i p_0 = 1. \quad (7)$$

The configuration factor f indicates the fraction of the free surface available for sliding and has the same forms as in the treatment of sliding during the impact of a particle – with the only exception: the steric hindrance factor is regarded as generally different from that one in the previous case and will be denoted by β' .

The over-all probabilities of the particular movements in the i -th step are then given by

$$\begin{aligned} {}^i p_{s,t} &= {}^i p_s f / [{}^i p_d + {}^i p_m + ({}^i p_s - {}^i p_m) f] \quad (\text{sliding}), \\ {}^i p_{m,t} &= {}^i p_m (1 - f) / [{}^i p_d + {}^i p_m + ({}^i p_s - {}^i p_m) f] \quad (\text{migration}), \\ {}^i p_{d,t} &= {}^i p_d / [{}^i p_d + {}^i p_m + ({}^i p_s - {}^i p_m) f] \quad (\text{desorption}), \end{aligned} \quad (8)$$

where ${}^i p_{s,t} + {}^i p_{m,t} + {}^i p_{d,t} = 1$.

The mean residence time of the particle in the i -th migration jump will be given by

$$1/\bar{i}_i = v [{}^i p_d + {}^i p_m + ({}^i p_s - {}^i p_m) f]. \quad (9)$$

It is assumed that practically all particles that have slid will be trapped on the free surface. The possibility of detachment from the surface after sliding may be expressed by ${}^i p_t$ which multiplies ${}^i p_{s,t}$, and by adding the term $(1 - {}^i p_t) {}^i p_{s,t}$.

In case there are k occupied sites in the neighbourhood of the site under consideration with m_j groups in j vicinal positions, then $k = \sum_j m_j$ and the configuration factor f is given by

$$z(1 - f) = \sum_{j=1}^k (j - 1 + \beta') m_j. \quad (10)$$

The number of ways of arranging elements is then

$$Z(m_j) = z \frac{(\sum_j m_j - 1)!}{\prod_j (m_j!)} \binom{z - 1 - \sum_j m_j}{m_j - 1}. \quad (11)$$

In view of the different denominators for various configurations, the necessary summations represent rather complex expressions. A substantial simplification can be obtained only if the probability of migration in case of a fully occupied vicinity ${}^i p_m$ approximately equals the probability of sliding for an isolated occupied site ${}^i p_s$. For relatively low coverages when high values of the frequency factor are most abundant, the denominator in (8) and (9) can be expressed with a sufficient accuracy by $({}^i p_d + {}^i p_s)$; for a high degree of the surface coverage in which configurations with a densely covered neighbourhood of the site under consideration dominate and f thus acquires a low value, the denominator may be substituted by $({}^i p_d + {}^i p_m)$.

The sum of products of various ways of arranging $Z(m_j)$ (11) and of the individual probabilities (8), using (10) for the particular factors f for k occupied vicinal sites in the i -th migration step, then gives the over-all probability of the considered phenomenon

$${}^i p_{d,i}(k) = \binom{z}{k} {}^i p_d / ({}^i p_d + {}^i p_s), \quad (12a)$$

$${}^i p_{m,i}(k) = \left[\binom{z-2}{k-2} + \beta' \binom{z-2}{k-2} \right] {}^i p_m / ({}^i p_d + {}^i p_s), \quad (12b)$$

where ${}^i p_x$ denotes either ${}^i p_s$ or ${}^i p_m$, according to the degree of surface coverage.

The summation over k after the multiplication by the probability factor of the occurrence of k occupied sites, i.e. $\vartheta^k (1 - \vartheta)^{z-k}$, then gives the following expressions for the over-all probability that the particle which has remained after the i -th migration step on the surface of the adsorbed particle will move in a given direction

$$\begin{aligned} {}^i P_d &= {}^i p_d / ({}^i p_d + {}^i p_s) \quad (\text{desorption}), \\ {}^i P_m &= \vartheta [\beta' + \vartheta(1 - \beta') {}^i p_m] / ({}^i p_d + {}^i p_s) \quad (\text{migration}), \\ {}^i P_s &= \{ {}^i p_s - {}^i p_m \vartheta [\vartheta + \beta'(1 - \vartheta)] \} / ({}^i p_d + {}^i p_s) \quad (\text{sliding}). \end{aligned} \quad (13)$$

For high surface coverages and less accurately also for low coverages

$${}^i P_s = (1 - \vartheta) Y' p_m / ({}^i p_d + {}^i p_m), \quad (13a)$$

where $Y' = 1 + \vartheta(1 - \beta')$.

In order to obtain an expression in a closed form for the over-all probability of adsorption of a particle approaching the surface, this model needs further simplification. First, the probabilities in the individual migration steps will be regarded as equal to each other, secondly, the fact will be neglected that migration progresses with time so that the surface is simultaneously being covered by particles arriving

from the gaseous phase, *i.e.* ϑ increases. Both these assumptions will be reasonable approximations for low and medium coverages, as the mean number of migration steps will be small and, therefore, the mean lifetime of a particle adsorbed on the covered surface will be very short in comparison with the reciprocal value of the rate of surface coverage (for values of p_m not very low). Indeed, the mean number of migration shifts is given, in this approximation, by (assuming $p_s = p_m$)

$$\frac{P_m}{1 - P_m} = \frac{p_m \vartheta [\beta' + \vartheta(1 - \beta')]}{p_m(1 - \vartheta) [1 - \vartheta(1 - \beta')] + p_d} \quad (14)$$

This expression reveals that even for a half-covered surface the mean number of migration shifts is smaller than one migration step.

The corresponding mean lifetime of this state is given by the product of (9) and (14)

$$\bar{t}_{\text{migr}} = \frac{1}{\gamma} \frac{P_m}{(p_m + p_d)} \frac{\vartheta [\beta' + \vartheta(1 - \beta')]}{p_m(1 - \vartheta) Y' + p_d} \quad (15)$$

which is of the order of magnitude $\vartheta/\nu p_m(1 - \vartheta)$.

Further, it will be assumed that the configuration in the vicinity of the particle is not influenced by the location of the original adsorption. This is a very rough assumption which enables us to use in further calculations the mean value of p'_s from (4). An accurate stochastic calculation would need further specifications concerning the behaviour of adsorbed particles and would be very complicated. Markov chains would have to be used.

This simplification of the described model and its treatment makes it possible to estimate the over-all probability of trapping an incoming particle on the free surface. Because of the assumptions made above, the particles adsorbed on the occupied surface need not be considered. The above mentioned probability is thus composed of the contribution of the primary trapping $p_0(1 - \vartheta)$, of the primary sliding with subsequent trapping $\alpha p_s \vartheta(1 - \vartheta) Y$, and, finally, of the sum of migration contributions resulting in

$$\frac{(1 - \vartheta) \vartheta Y' \alpha' [1 - p_s(1 - \vartheta) Y]}{(1 - \vartheta) Y' + p_d/p_m}$$

Thus the probability of adsorption is obtained as

$$P_{\text{ads}} = (1 - \vartheta) \left\{ p_0 + \vartheta \left[\frac{(1 - \vartheta) Y Y' p_s (\alpha - \alpha') + Y' \alpha' + \alpha p_s p_d / p_m Y}{(1 - \vartheta) Y' + p_d / p_m} \right] \right\} \quad (16)$$

This expression derived from a simple model with additional simplifications and approximations contains not less than seven independent parameters and is thus very

flexible in correlating the experimental data. Together with this flexibility, however, the uncertainty in the correctness of the used model increases. This is in agreement with the argument mentioned in the Introduction of this paper. The general feature of this model is that the decrease of the efficiency of trapping on the surface with the increasing coverage is at the beginning smaller than that one given by the simplest Langmuir model (proportionality to $(1 - \vartheta)$). Qualitatively, this decrease corresponds indeed to the observed behaviour in many cases. For very high coverages a steep drop in the efficiency of adsorption occurs. If the probability of adsorption on the free surface p_0 is low, this model allows for obtaining curves with a maximum of the adsorption probability in dependence on the degree of the surface coverage. Several typical graphical representations as foreseen by (16) are given in Fig. 1 and Fig. 2. It can be seen from these figures that the influence of sliding and migration takes place up to high surface coverages. Thus, this model cannot be used to explain experimental data on systems exhibiting a high adsorption efficiency at low surface coverages; in this case a sharp decrease starts at medium surface coverages. Also, this model cannot be used to interpret the often observed S-shaped curves of the adsorption efficiency.

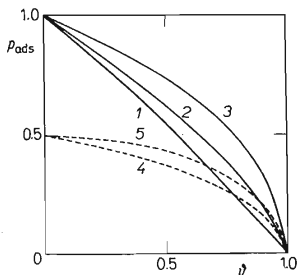


FIG. 1

Dependence of the Probability of Adsorption on the Surface Coverage

$p_d/p_m = 0.1$; $\alpha = 0.8$; $p_s = 0.25$ (for curve 5 0.5); $\beta = \beta' = 1.0$ (for curve 5 0.5); solid curves $p_0 = 1.0$ dashed curves $p_0 = 0.5$; α' : 1 0.0; 2, 4, 5 0.2; 3 0.5.

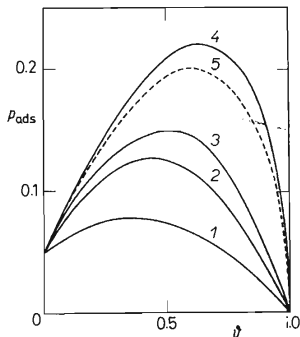


FIG. 2

Dependence of the Probability of Adsorption on the Surface Coverage

$p_d/p_m = 0.1$; $\alpha = 0.8$; $p_0 = 0.05$; $p_s = 0.5$ (for curve 1 0.25); solid curves $\alpha' = 0.0$; dashed curves $\alpha' = 0.2$; $\beta = \beta'$: 1 and 2 1.0; 3, 4, and 5 0.5; curve 5 gives P_{corr} for $p_v = 0.1$; $k_2/k_1 = 0.01$.

In the treatment reported here the influence of redesorption was not considered; this effect will decrease the observed effective adsorption efficiency. It is to be noted in this connection that besides the desorption due to fluctuations in energy distribution, the desorption activated directly by adsorption of particles with a subsequent release of energy has to be considered, too. For this released energy, the probability of harmless dissipation is the lower, the higher is the local coverage. Therefore, the higher the surface coverage, the higher will be the magnitude of this contribution to desorption. In general, a maximum will be reached at a certain surface coverage and then the magnitude will decrease because of a lower effective impacting efficiency of the incoming particles. Let us consider a simple model in which this secondary desorption is proportional to the number of adsorbed particles and to an unspecified power of the surface coverage through a proportionality constant p_v . If the rate of impacts of particles on the surface is k_1 and the rate constant of the thermally excited desorption is k_2 , the expression for the corrected adsorption probability reads

$$P_{\text{corr}} = P_{\text{ads}}(1 - p_v\vartheta) - (k_2/k_1)\vartheta, \quad (17)$$

where P_{ads} is given by (16). An equilibrium state of adsorption is evidently reached at such a surface coverage at which $P_{\text{corr}} = 0$. This correction decreases the effective probability of adsorption mainly at higher values of the surface coverage and in the region of highest coverages its influence decreases again. However, the S-shaped curves cannot be obtained in this case for reasonable values of the activated desorption, either.

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REFERENCES

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