# Brief Communications

## Calculation of the sticking coefficient in the case of the linear adsorption isotherm

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The expression of the sticking coefficient for the linear adsorption isotherm was derived. The sticking coefficient is an increasing temperature function and directly related to the entropy factor. The limits of applicability of the derived equation are discussed.

**Key words:** sticking coefficient, adsorption, linear adsorption isotherm.

The sticking coefficient ($s$) is a term in the adsorption rate constant. Therefore, the knowledge of its numerical value or the pattern of its dependence on the state parameters of the adsorption system is necessary for the theoretical study (simulation) of adsorption processes. Both classical and quantum-chemical approaches[1—3] are used for the calculation of $s$. Some interesting results can be obtained by studying the very general properties of the functional dependence of the amount adsorbed (directly related to $s$) on the state parameters.

Let us restrict our consideration by an equilibrium process at the solid—gas interface, and the solid surface will be considered as energetically homogeneous. In the case of one-component adsorption when the system experiences no mechanical or electromagnetic effects and the only processes in the system are adsorption/desorption, the amount adsorbed ($a$) is a continuous function of the adsorbate pressure ($p$) and temperature ($T$): $a = a(p,T)$. In addition, let us assume that adsorption involves an infinitely low amount of the adsorbate. This makes it possible to accept the isosteric heat of adsorption ($q_{st}$) as the heat effect of adsorption. In the initial region of surface coverages where the adsorption isotherm is described, as a rule, by a straight line, this assumption is warranted.

It is evident from the general considerations that the amount adsorbed is given by the formula

$$a = Ws\tau, \qquad (1)$$

where $W$ is the number of collisions of molecules with the surface unit per time unit, $\tau$ is the average residence time of a molecule on the surface. The following expression is known for the number of collisions of molecules with the surface: $W = p/(2\pi mkT)^{0.5}$, where $m$ is the weight of the

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molecule, and $k$ is the Boltzmann constant. The time $\tau$ is estimated from the Frenkel equation

$$\tau = \tau_0 \exp\left(\frac{E_d}{RT}\right),$$

where $E_d$ is the activation energy of desorption that will be considered as temperature-independent, $\tau_0$ is the pre-exponential factor, and $R$ is the universal gas constant. In the form of the Frenkel equation given above the exponent contains the $E_d$ value rather than the heat of adsorption. This form has been described previously[4] and is based on the assumption that the $\tau^{-1}$ value can be considered as the desorption rate constant. The pre-exponential factor is temperature-dependent. However, this dependence is much weaker than the exponential dependence and is usually neglected, accepting $\tau_0$ = const.

The following relationship is known to be valid for the $a = a(p,T)$ function of two variables:

$$\left(\frac{\partial p}{\partial T}\right)_a = -\frac{(\partial a/\partial T)_p}{(\partial a/\partial p)_T}. \tag{2}$$

The partial derivatives in the right part of Eq. (2) can be expressed using Eq. (1) through the corresponding $W$, $s$, and $\tau$ variables. In the framework of the accepted assumption, the two last variables are functions of $T$ only. As can easily be shown, the following relationships are valid: $(\partial W/\partial p)_T = W/p$, $(\partial W/\partial T)_p = -W/2T$, and $\mathrm{d}\tau/\mathrm{d}T = -\tau E_d/(RT^2)$. Then

$$\frac{1}{p}\left(\frac{\partial p}{\partial T}\right)_a = \left(\frac{\partial \ln p}{\partial T}\right)_a = \frac{E_d}{RT^2} + \frac{1}{2T} - \frac{1}{s}\frac{\mathrm{d}s}{\mathrm{d}T}.$$

By definition, $(\partial \ln p/\partial T)_a = q_{st}/(RT^2)$ (we accept that $q_{st}$ is temperature-independent). Putting necessary insertions and taking into account that the $(E_d - q_{st})$ difference is equal to the activation energy of adsorption ($E_a$), we have

$$\frac{1}{s}\frac{\mathrm{d}s}{\mathrm{d}T} = \frac{E_a}{RT^2} + \frac{1}{2T},$$

and the solution of this equation gives

$$s(T) = IT^{0.5}\exp\left(-\frac{E_a}{RT}\right), \tag{3}$$

where $I$ is the integration constant. Inserting Eq. (3) into Eq. (1) gives the qualitatively reasonable form of the adsorption isobar, *i.e.*, $p$ decreases with an increase in $T$ according to the $\exp(q_{st}/(RT))$ law.

Inserting function (3) and expressions for $W$ and $\tau$ into Eq. (1) and taking into account that the $a/p$ ratio is the adsorption equilibrium constant $K$ give the equation

$$K = \frac{I\tau_0}{(2\pi mk)^{0.5}}\exp\left(\frac{q_{st}}{RT}\right). \tag{4}$$

The $K$ constant can be presented as the product of the enthalpic $\exp(q_{st}/(RT))$ and entropic $\exp(\Delta S°/R)$ exponential factors.[5] Substituting this product into Eq. (4) instead of $K$ permits the mutual cancellation of the enthalpic factors in the right and left parts of the equality. As a result, we obtain the expression for $I$

$$I = \frac{(2\pi mk)^{0.5}}{\tau_0}\exp\left(\frac{\Delta S°}{R}\right),$$

where $\Delta S°$ is the change in the standard differential entropy upon adsorption. It is important that, when the $K$ equilibrium constant is expressed through the standard thermodynamic values, the $(K/K_0)$ ratio is used instead of the constant itself, where $K_0 = (a_0/p_0)$ under the condition that $a_0$ and $p_0$ are equal to unity, *i.e.*, the unit denominator with the dimensionality $K$ is used. The $K_0$ value is usually, as in this case, omitted. The resulting expression for $s$ is as follows:

$$s(T) = \frac{(2\pi mkT)^{0.5}}{\tau_0}\exp\left(\frac{-E_a}{RT}\right)\exp\left(\frac{\Delta S°}{R}\right). \tag{5}$$

In the case of activationless adsorption when $E_a = 0$, the equation obtained allows the calculation of the sticking coefficient from the data of equilibrium measurements only (determination of the adsorption entropy). In this case, $\tau_0$ can be estimated by the statistical thermodynamics.[2,6] The excessive adsorption is measured[7,8] by standard methods (gravimetric, volumetric, chromatographic) suitable for experimental studies of the adsorption equilibrium. The data are the basis for calculations of the excessive thermodynamic characteristics of adsorption.[7] In this work, we use the absolute value of the amount adsorbed (Eq. (1)). At the same time, the difference of the excessive and absolute values is negligible, as a rule, in the region of partial pressures of the adsorbate where the linear adsorption isotherm is observed, and the experimentally obtained excessive values can be used in calculations.

In conclusion, we consider the restrictions related to the applicability of Eq. (5). An unlimited increase in $s$ with an increase in $T$ contradicts the definition of the sticking coefficient, according to which $s \le 1$. The reason lies in the assumption of the form of the $s(T)$ and $\tau(T)$ functions. When deriving Eq. (3) we assumed that $s$ and $\tau$ are continuous, differentiated functions of $T$. In fact, these functions are confined to the limiting temperature of surface existence, above which they lose the physical meaning. The model discussed is confined in practice to a lower temperature, *viz.*, the melting point. The functions considered can exhibit the anomalous behavior near the melting point. For example, the Frenkel equation corresponds to the case when the amplitude of vibrations of the surface atoms of the solid is negligible compared to the amplitude of vibrations of the adsorption bond. When the temperature increases, especially near the melting point, the amplitude of vibrations of the lattice atoms becomes comparable with the corresponding amplitude of the adsorbed species. The application of the Frenkel equation is invalid in this situation. At high temperatures (even at those far from the melting point), the exponential factor of the Frenkel equation can be so low that the dependence of $\tau_0$ on $T$ becomes significant.

The region of application of Eq. (5) is also confined to low temperatures. Near the absolute zero where the quantum effects become discernable, the statements of the classical thermodynamics and kinetic theory of gases, adapted to put forward this formula, become invalid.

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