RATE OF ADSORPTION TO AND DESORPTION FROM A LANGMUIR SURFACE: THE CASE OF ZERO ACTIVATION BARRIER TO ADSORPTION WITHOUT DISSOCIATION

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Desorption from a Langmuir surface, pre-exponential factor for desorption rate constant

Many rate constants of elementary steps on single crystals have been measured. Their pre-exponential factors can now be compared to those calculated by transition state theory. Such a calculation is presented in this Letter with due attention to microscopic reversibility, standard states, and configurational entropy.

A classical result of gas kinetic theory is that the rate of adsorption v_a expressed in events cm^{-2} s^{-1} in the absence of an activation barrier is that of the rate of collision v_c times a sticking probability s:

$$v_a = sv_c = s\frac{\bar{v}}{4}[M] \tag{1}$$

where $[M]$ is the number density of molecules M in the fluid phase and ν is the mean molecular speed. In order of magnitude, $\nu/4$ is $\sim 10^4$ cm s^{-1}.

On the other hand, it is known [1] that the above result obtains from transition state theory, when the transition state still possesses two translational degrees of freedom parallel to the surface and when the internal degrees of freedom of M are unchanged in this transition state. Eq. (1) follows directly by assuming a standard state of 1 molecule cm^{-3} and of 1 molecule cm^{-2} in the fluid phase and in the transition state respectively. As usual the choice of standard states is a matter of convenience. In Langmuir exclusion site kinetics $s = s_0\ (1 - \theta)$ where s_0 is the sticking probability at zero fractional coverage θ. The sticking probability at zero coverage is frequently taken to be a transmission coefficient in the spirit of transition state theory [2]. For adsorption without activation barrier, s_0 is of the order of unity.

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For a Langmuir surface with identical sites * for localized adsorption, the rate v_d of reverse unimolecular desorption of M adsorbed on site *

$$M^* \rightarrow M + {}^*,$$

will now be obtained with due attention to the principle of microscopic reversibility when there is no activation barrier for adsorption.

The entropy S_a in the adsorbed phase is

$$S_a = S_{a,int} - R \ln \frac{\theta}{1-\theta} \tag{2}$$

where the first term on the right is the *internal* entropy of M^* depending only on temperature, and the second term is the configurational entropy on the Langmuir surface [3,4].

From the principle of microscopic reversibility, it is mandatory for the *desorption problem* to choose as standard state (superscript $^{\ominus}$) of surface concentration a number density of 1 molecule cm^{-2} as was done for the *adsorption problem*. If for the sake of clarity, without loss of generality, we assume a surface number density of sites $[L]$ many orders of magnitude larger than 1 cm^{-2}, $\theta \cong L^{-1}$ and $1 - \theta \cong 1$, so that from eq. (2):

$$S_a^{\ominus} \cong S_{a,int} - R \ln L^{-1}.$$

Again, from the principle of microscopic reversibility, the transition state for desorption possesses two translational degrees of freedom, as it does for the reverse process of adsorption without an activation barrier. Thus, for the transition state ‡ at its standard state $^{\ominus}$,

$$S^{\ominus\ddagger} = S^{\ominus\ddagger}_{2D,trans} + S^{\ddagger}_{int}.$$

where $S^{\ddagger}_{int}$ is the entropy due to the internal degrees for freedom of $M^{\ddagger}$. We know [1] that according to the Sackur-Tetrode equation for translational entropy in two dimensions:

$$\frac{S^{\ddagger}_{2D,trans}}{R} = 2 + 2 \ln \frac{kT/h}{\bar{v}/4} + \ln A \tag{3}$$

where $kT/h \cong 10^{13}$ s^{-1} with the usual notations and A is the area available per molecule.

The *standard* value, $S^{\ominus\ddagger}_{2D,trans}$, corresponds to the already chosen state of A, 1 molecule $cm^{-2} = 1/A$. Thus at the standard state $\ln A = 0$ and eq. (3) becomes:

$$\frac{S^{\ominus\ddagger}_{2D,trans}}{R} \cong 2 + 2 \ln 10^9.$$

Finally

$$\exp\left(\frac{S^{\ominus\ddagger}_{2D,trans}}{R}\right) \cong 10^{19}.$$

Transition state theory gives for the rate of desorption v_d:

$$v_\mathrm{d} = s_0 \frac{kT}{h} \mathrm{e}^{\Delta S^{\ominus\ddagger}/R} \mathrm{e}^{-\Delta H^{\ominus\ddagger}/RT} [M^*]$$

where s_0 is the same transmission coefficient as for adsorption, again to respect the principle of microscopic reversibility, while $\Delta S^{\ominus\ddagger}$ and $\Delta H^{\ominus\ddagger}$ are the changes in *standard* entropy and enthalpy respectively to form the transition state ‡ from reactant M^*.

Thus:

$$\Delta S^{\ominus\ddagger} = S^{\ominus\ddagger} - S_\mathrm{a} \cong S^{\ominus\ddagger}_\mathrm{2D,trans} + S^{\ddagger}_\mathrm{int} - S_\mathrm{a,int} + R \ln L^{-1}$$

$$\text{and } \exp(\Delta S^{\ominus\ddagger}/R) \cong 10^{19} \times L^{-1} \exp(\Delta S^{\ddagger}_\mathrm{int}/R)$$

where $\Delta S^{\ddagger}_\mathrm{int}$ is the change in internal entropy (vibrational and rotational) to form the transition state from adsorbed reactant. Finally then the pre-exponential factor for the rate constant for desorption is equal to:

$$s_0 \frac{kT}{h} \mathrm{e}^{\Delta S^{\ominus\ddagger}/R} \cong s_0 \times 10^{13} \times 10^{19} \times L^{-1} \mathrm{e}^{\Delta S^{\ddagger}_\mathrm{int}/R}. \qquad (4)$$

The pre-exponential factor of eq. (4) depends on the value of s_0 and ΔS_int. With an order of magnitude value for $[L] = 10^{15}$ cm^{-2} and with reasonable values for s_0 and ΔS_int, it is in agreement with experimental results [5] pertaining to the desorption of CO from metal surfaces on which CO is adsorbed without an activation barrier. Experimentally, the pre-exponential factor of the rate constant for the desorption of adsorbed CO is found to vary between 10^{13} and 10^{17} s^{-1} [5]. Values in excess of $\sim 10^{13}$ s^{-1} were difficult to understand until recently. These experimental results led Menzel to statements [6] that are clarified in this Letter. The merit of Menzel has been to stress the importance of microscopic reversibility in adsorption and desorption. In our treatment, this is observed. Indeed, in summary, noting that $[M^*] = \theta[L]$:

$$v_\mathrm{a} = s_0 \frac{kT}{h} \exp \frac{1}{R} \left(S^{\ominus\ddagger}_\mathrm{2D,trans} + S^{\ddagger}_\mathrm{int} - S_{M,\mathrm{int}} - S^{\ominus}_\mathrm{3D,trans} \right) \times [M](1-\theta)$$

$$v_\mathrm{d} = s_0 \frac{kT}{h} \exp \frac{1}{R} \left(S^{\ominus\ddagger}_\mathrm{2D,trans} + S^{\ddagger}_\mathrm{int} - S_\mathrm{a,int} + R \ln L^{-1} \right) \exp(-\Delta H^{\ominus\ddagger}/RT) \times \theta[L].$$

Dividing these two expressions side by side and noting that $v_\mathrm{a} = v_\mathrm{d}$ at equilibrium, we obtain, as we should, the Langmuir adsorption isotherm:

$$\frac{\theta}{1-\theta} = K_\mathrm{a}[M]$$

with

$$K_\mathrm{a} = \exp(\Delta S^{\ominus}_\mathrm{a}/R) \times \exp(-\Delta H^{\ominus}_\mathrm{a}/RT)$$

where $\Delta H^{\ominus}_\mathrm{a} = -\Delta H^{\ominus\ddagger}$ since there is no activation barrier to adsorption, and $\Delta S^{\ominus}_\mathrm{a} = S_\mathrm{a,int} - R \ln L^{-1} - S_{M,\mathrm{int}} - S^{\ominus}_\mathrm{3D,trans}$.

Our treatment has used the thermodynamic language of transition state theory with entropy instead of partition function. Of course both languages are equivalent, but with partition functions, standard states are usually left unspecified. In our treatment, they are spelled out and made consistent with the requirements of the principle of microscopic reversibility. A review of the kinetic treatment of other elementary steps on Langmuir surfaces following the treatment of this paper is in preparation [7].

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