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Variation of the τ_0 terms in the Frenkel's formula

Wahania czynnika τ_0 we wzorze Frenkla

ABSTRACT

Vibrations of an adsorbed molecule are briefly discussed. The mean time of adsorption as well as the so-called "Frenkel's constant", τ_0 , are derived from statistical physics. For τ_0 the following approximate formula was derived: $\tau_0 = \pi r_0 (2m/Q)^{1/2}$, where r_0 is mean adsorbent-adsorbate distance, m is the molal mass of adsorbed molecule, and Q is adsorption energy. Calculations for H_2 , N_2 , O_2 , CO and Ar show that τ_0 varies from $4 \cdot 10^{-14}$ to 10^{-12} s.

1. INTRODUCTION

For most molecules or atoms adsorbed on metallic surfaces, there is a large influence of the adsorbed layer on the work function of the base

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metal of interest [1]. When the ionization potential of the adsorbate atoms is of the order of, or not too much higher than the work function of the adsorbent metal, the effect of a monolayer of these atoms is to decrease the work function of the composite surface. Such situation occurs for monolayers of alkali metals, some rare earth metals and thorium or zirconium on tungsten. If the adsorbed atom may exist stably as negative ion (e.g. oxygen, sulfur) it can increase the work function of a metal. In both cases, the influence of the adsorbed atoms on the work function will change the physical properties of a surface dramatically. Therefore, apart from knowing the sort of adsorbed molecules, it is necessary to know either the surface coverage, θ , or the mean time of adsorption, τ .

The formula for the mean time of adsorption, τ , derived by J. Frenkel [2] on the basis of statistical mechanics has been quoted and used very frequently, owing to its simplicity. This well recognized formula is:

$$\tau = \tau_0 \exp\left(\frac{Q}{kT}\right), \quad (1)$$

where τ is the mean time of adsorption (reciprocal of specific rate of desorption), Q is desorption energy, k is Boltzmann constant and T is temperature. It was usually assumed by experimenters that Q may be considered as parameter representing the chemical specificity of each particular reaction, whereas τ_0 was treated as a kind of universal constant, with a value close to 10^{-13} s.

This “constant” was originally treated as a reciprocal of the vibration frequency of adsorbed molecule along the direction perpendicular to the surface. However, later experimental determinations showed that the value of τ_0 seems to be larger than 10^{-13} s, quite frequently for a few orders of magnitude, depending on gas and surface species, temperature, shape of the potential and other physical conditions [3]. It was also noticed that “ τ_0 has no relation to the time of vibration of the constituent molecules or atoms of the adsorbing surfaces, but is often of the same order of magnitude” (from [7], page 32) and therefore relating of τ_0 to bulk physical properties of the surface was recognized as a rough estimate. It is the purpose of this short paper to discuss briefly the nature of vibrations of adsorbed molecule as well as τ_0 .

2. DERIVATION OF THE FRENKEL'S FORMULA

Let us imagine the volume V filled with gas molecules. Let S be the surface remaining in contact with gas. We assume the equilibrium conditions, at which the number of adsorbed molecules, N_a , and N (the total number of molecules in volume V) remain constant. The ratio N_a/N may be calculated by means of the statistical partition functions as follows [4]:

$$\frac{N_a}{N} = \frac{Z_a}{Z_{trans}} = \frac{Z_x Z_y Z_{vib}}{Z_{trans}}, \quad (2)$$

where $Z_x Z_y$ is equal to $S(2\pi mkT/h^2)$. Since the translational partition function of the free molecules is calculated from a common zero energy level, the desorption energy, Q , has to be added to each transitional energy level, E_i , in calculation of Z_{trans} . Therefore:

$$Z_{trans} = \sum_{i=1}^{\infty} e^{-\frac{Q+E_i}{kT}} = e^{-\frac{Q}{kT}} \sum_{i=1}^{\infty} e^{-\frac{E_i}{kT}} = e^{-\frac{Q}{kT}} V \left(\frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}}. \quad (3)$$

The number of desorbing molecules per unit of time is:

$$\frac{dN}{dt} = \frac{N_a}{\tau}, \quad (4)$$

whereas the number of molecules being adsorbed is:

$$\frac{dN}{dt} = \frac{1}{2} S \bar{v} \frac{N}{V}, \quad (5)$$

where \bar{v} is the mean velocity of a free molecule in direction perpendicular to the surface. In equilibrium conditions, the number of adsorbed molecules per unit of time is equal to the number of desorbed molecules. From equations (4), (5) and (2) we obtain:

$$\tau = \frac{2V N_a}{S \bar{v} N} = \frac{2V Z_x Z_y Z_{vib}}{S \bar{v} Z_{trans}}. \quad (6)$$

The mean velocity, \bar{v} , may be calculated by use of the Maxwell distribution:

$$\bar{v} = \frac{\int_0^{\infty} v e^{-\frac{mv^2}{2kT}} dv}{\int_0^{\infty} e^{-\frac{mv^2}{2kT}} dv} = \frac{2 \frac{kT}{m}}{\sqrt{\frac{2\pi kT}{m}}} = \sqrt{\frac{2kT}{\pi m}}. \quad (7)$$

Substituting (7) to (6) we obtain:

$$\tau = \frac{V Z_x Z_y Z_{vib}}{S Z_{trans}} \sqrt{\frac{2\pi kT}{m}} = \frac{Z_{vib}}{e^{-\frac{Q}{kT}} \sqrt{\frac{2\pi mkT}{h^2}}} \sqrt{\frac{2kT}{\pi m}} = \frac{h}{kT} Z_{vib} e^{\frac{Q}{kT}}. \quad (8)$$

By denoting $\tau_0 = \frac{h}{kT} Z_{vib}$, we obtain the well recognized formula (1) derived by Frenkel [2] over 70 years ago. A similar derivation based on statistical physics was found by de Boer [7].

3. DISCUSSION

The Z_{vib} term may be calculated as a sum of all the energy levels of the adsorbed molecule being trapped in a parabolic potential well:

$$Z_{vib} = \sum_{i=1}^{\infty} e^{-\frac{E_i}{kT}}, \quad (9)$$

where $E_i = ih\nu + \frac{1}{2}h\nu$ is the energy of level i . Therefore:

$$Z_{vib} = \sum_{i=1}^{\infty} e^{-\frac{ih\nu + \frac{1}{2}h\nu}{2kT}} = e^{-\frac{h\nu}{2kT}} \sum_{i=1}^{\infty} e^{-\frac{ih\nu}{kT}}. \quad (10)$$

Since $e^{-\frac{h\nu}{kT}} < 1$, the term $\sum_{i=1}^{\infty} e^{-\frac{ih\nu}{kT}}$ tends to $1/\left(1 - \exp\left(-\frac{h\nu}{kT}\right)\right)$, and:

$$Z_{vib} = \frac{e^{-\frac{h\nu}{2kT}}}{1 - e^{-\frac{h\nu}{kT}}}. \quad (11)$$

In high temperatures and for relatively low values of vibration energy (e.g. in case of most molecules on metallic surfaces) we assume $h\nu \ll kT$. Therefore, denoting $U = h\nu/kT \ll 1$ and knowing that $e^{-U} \approx 1 - U$ for small U we obtain:

$$Z_{vib} = \frac{e^{-\frac{U}{2}}}{1 - e^{-U}} \rightarrow \frac{1 - \frac{U}{2}}{1 - (1 - U)} \approx \frac{1}{U}. \quad (12)$$

We may now calculate τ_0 as:

$$\tau_0 = \frac{h}{kT} Z_{vib} = \frac{h}{kT} \frac{kT}{h\nu} = \frac{1}{\nu}. \quad (13)$$

It is now clear, that in the case discussed above τ_0 may safely be treated as a period of vibrational oscillation, which is the reciprocal of frequency of vibrations perpendicular to the surface.

This frequency may be estimated from the potential energy of the adsorbed state as a function of distance from the surface. Usually, the Lennard-Jones potential is used:

$$E(r) = 4\pi\epsilon nr_0^3 \left[\frac{1}{45} \left(\frac{r_0}{r} \right)^9 - \frac{1}{6} \left(\frac{r_0}{r} \right)^3 \right], \quad (14)$$

where r_0 is the bond length, ϵ is certain energy the value of which depends on the molecular species and n is mean atomic density of the adsorbing surface [5]. There are several papers dedicated to measurement of Q for various molecules on various surfaces. Unfortunately, the values of r_0 , albeit necessary, are extremely rarely seen in literature. A.A. Adamson expressed this problem in his recent book [6]:

The subject [of bond formation] was hampered by scarcity of direct experimental information. Adsorption energies can be determined, of course, but adsorbent–adsorbate bond lengths are generally not known.

For this reason only a general look at the shape of potential as well as at the value of v may be performed here. First, in order to simplify the calculations, we will approximate the Lennard-Jones potential (14) by a parabolic potential. Having v and τ_0 calculated this way, we will discuss the dependence of these values on hypothetical r_0 .

The approximate value of v may be found from simple calculations. Assuming that the molecule trapped in a potential well may be treated as a harmonic oscillator, the energy of a molecule is:

$$E(r) = \frac{1}{2} k_p r^2 \quad (15)$$

where k_p is the proportionality constant between the applied force and distance from the equilibrium point, $F = -k_p r$. Molecule may be treated that way as long as we assume the quasi-elastic character of vibrations, which is true for small amplitudes. The frequency of such vibrations is:

$$v = \frac{1}{2\pi} \sqrt{\frac{k_p}{m}}. \quad (16)$$

Additionally, we assume that the shape of the parabolic potential is such, that $E(r) = Q$ for $r = r_0$. Therefore, from equation (15) one obtains:

$$k_p = \frac{2Q}{r_0^2}. \quad (17)$$

From the last two equations and (13), the value of τ_0 may be calculated:

$$\tau_0 = \pi r_0 \sqrt{\frac{2m}{Q}}. \quad (18)$$

The values of τ_0 calculated on the basis of Q values after [5] for various molecules adsorbed on tungsten surface are listed in Table 1.

Table 1. Calculated by authors τ_0 values for different molecules adsorbed on tungsten surface, for $r_0 = 1 \text{ \AA}$
Obliczone przez Autorów wartości parametrów τ_0 w przypadku różnych molekuł zaadsorbowanych na wolframie

Molecule	O ₂	H ₂	N ₂	CO	Ar
Molal mass [10 ⁻³ kg]	32	2	28	28	40
Q [kJ/mol]	615	310	649	419	7.96
τ_0 [ps]	0.10	0.04	0.09	0.12	1.00

One may see from Table 1 that the calculated τ_0 values vary by more than one order of magnitude, from $4 \cdot 10^{-14}$ to 10^{-13} s.

4. CONCLUSION

The value of τ_0 in the Frenkel's formula for mean desorption time by no means can be treated as a universal constant. We propose estimation of this value by means of approximate equation (18). According to this equation, τ_0 is related to the mass of adsorbed molecule, heat of desorption and adsorbent-adsorbate distance.

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REFERENCES

- [1] Smith L.P., *Thermionic Emission. CRC Handbook of Physics*, 74-82, Boca Raton FL (USA) 1985.
- [2] Frenkel J., *Zeit. Phys.*, (1924) 25, 287-291.
- [3] Ageev V.N. Ustinov Y.K. and Ionov N.I., *Sov. Phys. Tech. Phys.*, (1965) 10, 851.
- [4] Landau L. and Lifszyc E., *Statistical Physics*, PWN, Warsaw 1959 [in Polish].
- [5] Hałas S., *Technology of High Vacuum*, PWN, Warszawa 1980 [in Polish].
- [6] Adamson A.A., *Physical Chemistry of Surfaces*, Wiley, New York 1990.
- [7] de Boer, *The Dynamical Character of Adsorption*, Oxford Univ. Press, Oxford 1953.

STRESZCZENIE

W artykule zanalizowano rolę drgań zaadsorbowanych cząsteczek na powierzchni metalu w polu sił wzajemnego przyciągania powierzchnia-cząsteczka. Wzór określający średni czas adsorbcji i stałą Frenkla został wyprowadzony na podstawie metod fizyki statystycznej. Wyprowadzono następujący wzór przybliżony: $\tau_0 = \pi r_0 (2m/Q)^{1/2}$, gdzie r_0 jest średnią odległością adsorbent-adsorbat; m – masą cząsteczkową; Q – energią adsorbcji. Obliczenia H_2 , N_2 , O_2 , CO i Ar wykazały, że τ_0 waha się w przedziale $4 \cdot 10^{-14}$ – 10^{-12} s.