THE DOUBLE ELECTRIC LAYER AT THE BOUNDARY OF AMORPHOUS BODIES CAUSED BY A DONOR-ACCEPTOR BOND

1961

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

V. P. SMILGA

THE DOUBLE ELECTRIC LAYER AT THE BOUNDARY OF AMORPHOUS BODIES CAUSED BY A DONOR-ACCEPTOR BOND

(Presented by Academician A. N. Frumkin, February 8, 1961)

In works ([1]) the role of double electric layers in the phenomena of adhesion of crystalline solids was investigated. However, for practice the greatest interest is presented by the study of the adhesion of polymers and amorphous bodies with their very complex and, generally speaking, irregular molecular structure. It is therefore necessary to study the regularities of formation of a double electric layer upon contact of polymers or amorphous bodies.

Let us suppose that the near-surface layer of one of the contacting bodies is saturated with donor molecules, and the other with acceptor molecules. The numbers of donors and acceptors per 1 cm^2 are respectively N_d and N_a. We introduce a certain averaged position of the donor and acceptor centers (see Fig. 1). The curve shows the energy of the electron; moreover, the energy well N_d corresponds to the main level of the electron in the donor, and N_a to that in the acceptor center; d_1 and d_2 are the distances of the donors and acceptors from the interface, and W_0 is the difference between the energy levels of the electron in the donor and acceptor centers. When the energy level of the electron in the acceptor center is situated lower than in the donor, the heat of reaction W_0 is a positive quantity.

The specific feature of the problem consists in the fact that the reaction proceeds over the whole surface, so that each donor–acceptor pair finds itself in the electrostatic field created by the other pairs that have already reacted. This field changes the difference between the energy levels of the electron, and the heat of reaction thus depends on the number of centers that have reacted. The difference between the potential energies of the electron in the donor and acceptor centers is determined by the expression

$$W(n) = W_0 - e\Delta V(n); \tag{1}$$

here $\Delta V(n)$ is the potential difference between the centers of the potential wells for the electron in the donor and acceptor centers, created by the field of the remaining donor–acceptor pairs that have already reacted.

Let us suppose, for definiteness, that the density of donor centers is less than that of acceptor centers ($N_d < N_a$). In what follows we shall assume that the acceptor centers are sufficiently densely arranged on the surface, so that the electron of a donor center passes to the nearest acceptor center, located opposite or "almost opposite"the donor. It should be pointed out that all further calculations remain almost unchanged also in the case when the electron of a given donor center can "choose" among several acceptors. We also note that everywhere below we assume that the electrons cannot move freely along the surface.

The equilibrium state of the system is determined from the condition of a minimum of the free energy as a function of the number of donor-acceptor pairs that have reacted. In other words, the free energy of the system is

$$F = F_0 + \Delta F(n) = F_0 + \Delta E(n) - T\Delta S(n) \tag{2}$$

in the state of equilibrium satisfies the condition $(\partial F/\partial n)_T = 0$; here n is the number of reacted pairs per 1 cm^2.

The increase of entropy in the reaction process is determined by the relation

$$\Delta S(n) = k \ln \frac{N_d!}{(N_d - n)!\, n!} \simeq k\left[N_d \ln N_d - (N_d - n)\ln(N_d - n) - n \ln n\right]. \tag{3}$$

Naturally, if the number of acceptors is smaller than the number of donors, then N_a should appear in formula (3) instead of N_d.

In the case where, for the electron of each donor center, there is a possibility of choosing among several acceptor centers, the expression for $\Delta S(n)$ is somewhat modified and, in the limiting case where the electron of any donor can be on any acceptor, takes the form

$$\Delta S(n) = k\left[\ln \frac{N_d!}{(N_d - n)!\, n!} + \ln \frac{N_a!}{(N_a - n)!\, n!}\right]. \tag{3a}$$

We shall mainly confine ourselves to the case in which formula (3) is valid, since all the characteristic features of the reaction are fully manifested in this model, and, as applied to real problems, the model is quite plausible. The change in the internal energy of the system is equal to: $\Delta E(n) = -n[W_0 - e\Delta V]$. Minimizing the free energy with respect to n, we obtain

$$\left(\frac{\partial F}{\partial n}\right)_T = -W_0 + e\Delta V(n) + en\frac{\partial \Delta V(n)}{\partial n} - kT \ln \frac{N_d - n}{n} = 0, \tag{4}$$

whence

Fig. 1

Figure 1: Fig. 1

$$\frac{n}{N_d - n} = \exp\left[\frac{W_0 - e\Delta V(n) - en\dfrac{\partial \Delta V(n)}{\partial n}}{kT}\right]. \tag{5}$$

To determine n, it is necessary to know the form of the function $\Delta V(n)$. If in the state of equilibrium the number of reacted pairs is sufficiently small, $\Delta V(n)$ is practically equal to zero; when n increases, the function $\Delta V(n)$ has, generally speaking, a rather complicated form, since it is necessary to take into account the discrete structure of the double layer. The problem of determining $\Delta V(n)$ is essentially identical with the problem of calculating the micropotential, which is of great importance for electrochemistry. It should be noted, however, that in our case it is hardly expedient to carry out a rigorous calculation of $\Delta V(n)$ with allowance for the discrete structure of the double layer, although this problem reduces to laborious but, in principle, quite simple calculations (see, for example, ([2])).

Fig. 1

Indeed, first, in considering a double layer with a discrete structure it is also necessary to propose some specific model (for example: the reacted pairs form a plane hexagonal lattice), so that the character of the function $\Delta V(n)$ still remains somewhat conditional. Second, when the number of reacted pairs is sufficiently large (and it is precisely this case that is of interest to us), one may think that, describing the double layer as a capacitor with charge "smeared out" over the plane, we shall obtain a sufficiently good approximation. Finally, at the present time, when experimental material on the study of the regularities of donor-acceptor bonding upon contact of solids is practically absent, it is hardly necessary to strive for deceptive rigor; rather, one should give a qualitative description of the process, and also estimate how real the influence of donor-acceptor reactions on adhesion forces may be.

The "plane capacitor" hypothesis fully satisfies these purposes. In this case $\Delta V(n)$ is equal to:

$$\Delta V(n) = \frac{4\pi en}{\alpha}\left(\frac{d_1}{\varepsilon_1} + \frac{d_2}{\varepsilon_2}\right).$$

The factor α is connected with the fact that $\Delta V(n)$ is determined only by the field of the "external" reacted pairs, while the part of the "smeared-out charge" associated with that donor-acceptor pair for which $\Delta V(n)$ is being determined should not be included in the calculation.

From elementary considerations it is clear that, so long as the charge densities are sufficiently large ($1/\sqrt{n} \approx d_1 + d_2$), α is a slowly varying function of n and,

Fig. 2.

Figure 2: Fig. 2.

in order of magnitude, is close to unity.

Taking into account the form of $\Delta V(n)$, we have

$$\frac{n}{N_d - n} = \exp\left[\frac{W_0 - e\beta V(n)}{kT}\right], \tag{6}$$

where

$$V(n) = 4\pi e n \left(\frac{d_1}{\varepsilon_1} + \frac{d_2}{\varepsilon_2}\right)$$

is the potential difference between the plates of the double layer, and $\beta = 2/\alpha$ is independent of n and, in order of magnitude, close to unity.

Fig. 2.

$$f = \frac{1}{1 + \exp\{-[W_0 - \gamma n]/kT\}}, \qquad N_{d_1} < N_{d_2},\ T_1 < T_2$$

As is seen from (6), in order to determine n one must solve a transcendental equation, which can be done graphically if definite values of the parameters are specified. One of our tasks is to estimate the order of magnitude of n; therefore reasonable assumptions should be made regarding the parameters, and we should see what values of n are obtained.

If we assume that $d_1 + d_2 \approx 5 \cdot 10^{-8}$—$10^{-7}$ cm, $W_0 \approx 0.5$—1 eV, $N_d \approx 10^{13}$—10^{14} cm^{-2}, and $\varepsilon_1 \approx \varepsilon_2 \approx 10$, then it is easy to verify that n is, in order of magnitude, equal to 10^{11}—10^{13}. Such values of n correspond to a double-layer charge density of 10^2—10^4 CGSE and can provide adhesion forces of the order of hundreds of kilograms per square centimeter.

Thus, one may think that, in a certain class of cases, the donor–acceptor bond and the double electric layer caused by it play a decisive role in adhesion phenomena. A necessary condition for the formation of a sufficiently dense double electric layer is the preliminary saturation of one of the reacting surfaces with donor functional groups, and the other with acceptor functional groups.

At present, a fairly large number of molecules and functional groups possessing donor or acceptor properties are known, and, by selecting appropriate pairs and saturating the surface with them, one may count on creating high adhesion. It should be emphasized that in the works of N. A. Krotova and L. P. Morozova ([4]) a dependence was observed of the density of the double electric layer and of the adhesion properties on the chemical modification of the surface.

In particular, it is known ([3]) that long molecules with conjugated bonds containing a nitrogen atom easily lose an electron, and it would be of interest to trace the adhesion properties of polymers with such functional groups.

Using (6), one can draw several curious conclusions about the nature of the process of double-layer formation. The specific feature of the reaction under consideration is that the process of double-layer formation is self-retarding. If from the very beginning the transfer of an electron from donor to acceptor is associated with absorption of energy ($W_0 < 0$) and the reaction is endothermic, then its endothermicity increases as the double layer forms. As a result, the equilibrium state is reached at smaller values of n than if the energy absorbed by the reaction were unchanged. If $W_0 > 0$, the reaction is initially exothermic. As the double layer forms, the heat

the reaction decreases, and it may turn out that even before equilibrium is reached the reaction changes from exothermic to endothermic (at the moment when $e\Delta V(n)$ becomes greater than W_0).

Introduce the notation $\gamma = 4\pi e^2 b \left(\frac{d_1}{\varepsilon_1} + \frac{d_2}{\varepsilon_2} \right)$ and rewrite (6) in the form

$$\frac{n}{N_d} = \frac{1}{1 + \exp\{-[W_0 - \gamma n]/kT\}}. \tag{7}$$

Considering n as a function of T, it is easy to see that if the root of equation (7) lies in the region $\gamma n < W_0$, then n decreases as T increases. Conversely, if the root of the equation lies in the region where $\gamma n > W_0$, then n is a monotonically increasing function of temperature. This can be shown most simply by examining equation (7) graphically (see Fig. 2). The root of the equation is determined by the point of intersection of the straight line $y = n/N_d$ with the curve defined by the right-hand side of (7).

As is seen from the graph, by increasing, all other conditions being equal, the initial concentration of donor centers, one can transform an exothermic reaction into an endothermic one.

This conclusion seems especially interesting, since it is possible that an analogous situation also arises in problems of chemisorption, when the latter is due to a donor–acceptor bond, as well as in problems connected with the formation of a double layer at a solid–electrolyte boundary.

In conclusion, let us note that if the change in entropy is determined by formula (3a), then, minimizing the free energy, instead of equation (5) we obtain

$$\frac{n^2}{(N_d - n)(N_a - n)} = \exp\left[\frac{W_0 - e\Delta V(n) - en\,\partial\Delta V(n)/\partial n}{kT} \right]. \tag{8}$$

I express my gratitude to B. V. Deryagin for his attention to this work.

Institute of Physical Chemistry
Academy of Sciences of the USSR

Received
19 I 1961

References

[1] V. B. Sandomirskii, V. P. Smilga, *Fiz. Tverd. Tela*, **1**, 2 (1960); B. V. Deryagin, V. P. Smilga, *DAN*, **121**, No. 5 (1958); V. P. Smilga, B. V. Deryagin, *DAN*, **122**, No. 6 (1958). [2] O. Esin, I. Shikhov, *ZhFKh*, **17**, 236 (1943). [3] S. Reid, *Excited States in Chemistry and Biology*, IL, 1960. [4] N. A. Krotova, L. P. Morozova, *DAN*, **129**, No. 1 (1959).

Note: Figure translations are in progress. See original paper for figures.