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Abstract

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ON THE CONDENSATION (STICKING) COEFFICIENT OF GAS MOLECULES DURING THEIR CHEMISORPTION ON A METAL SURFACE

(Presented by Academician A. N. Frumkin, 26 VI 1961)

Numerous works have been devoted to the experimental and theoretical study of the question considered here. However, only after Becker' s work (^{1}) was a series of works ($^{2-4}$) carried out, and experimental data were obtained both on the magnitude of the condensation (sticking) coefficient $\varkappa$ and on its dependence on the concentration n of adsorbed atoms or molecules. As a result of these works it was established that $\varkappa$ for the gases investigated (H_2, O_2, CO, N_2) is almost constant within a certain interval of variation of n and is always less than unity ($\varkappa \approx 0.5 \div 0.1$). With a further increase in n, the coefficient $\varkappa$ begins to decrease sharply and reaches values $\sim 10^{-3} \div 10^{-4}$.

A number of attempts (^{2,5}) are known to explain the dependence of the magnitude of $\varkappa$ on n, but they were not successful. All the authors proceeded from the assumption that the experimentally measured decrease of $\varkappa$ with increasing n occurs in reality.

The basis of the present work is the assumption that the condensation coefficient $\varkappa$ does not depend on the concentration n of adsorbed molecules. The experimentally observed decrease of $\varkappa$ with increasing n is associated with the evaporation of part of the adsorbed molecules because of the strong decrease in the heat of chemisorption with increasing n, as a result of the interaction of adsorbed molecules, the theory of which was developed by us in previous works (^{6}).

We shall distinguish between the condensation coefficient $\varkappa = dn/dN$ and the mean condensation coefficient $K = n/N$, where n is the total number of adsorbed molecules, and N is the number of molecules that have fallen on the metal surface during a given interval of time; moreover,

$$K = \bar{\varkappa} = \frac{1}{n}\int_0^n \varkappa\, dn. \qquad (1)$$

Fig. 1

Figure 1: Fig. 1

For the formation of an electronic bond with the surface, apparently, some time is required, longer than the time of collision of the molecule with the surface. Therefore we consider that chemisorption is always preceded by physisorption, which is characterized by its own condensation coefficient $\varkappa_\phi$. Correspondingly, chemisorption is characterized by its own coefficient $\varkappa_{\mathrm{x}}$. In experiment the apparent condensation coefficient during chemisorption was usually measured,

$$\tilde{\varkappa}_{\mathrm{x}} = \frac{d(n - n_{\mathrm{u}})}{dN} = \frac{dn_{\mathrm{x}}}{dN}$$

or the mean apparent condensation coefficient during chemisorption $\tilde{K}_{\mathrm{x}} = n_{\mathrm{x}}/N$, where $n_{\mathrm{x}} = n_{\mathrm{v}} - n_{\mathrm{u}}$. Here n_{x} is the number of chemisorbed molecules that have remained on a unit surface (i.e., the concentration), and n_{u} is the number that evaporated during the same time.

Let a flux of molecules dN/dt fall on the surface; then the change in the concentration of physisorbed molecules dn_ϕ/dt will be

$$\frac{dn_\phi}{dt} = \chi_\phi \frac{dN}{dt} - n_\phi a e^{-q_\phi/kT} - n_\phi b e^{-\varepsilon/kT}. \qquad (2)$$

Here the second and third terms on the right-hand side, according to the theory of absolute reaction rates (7), are respectively equal to the flux of evaporating physisorbed molecules and to the flux of molecules passing from the physisorbed into the chemisorbed state; q_ϕ is the heat of physisorption; ε is the activation energy for the transition from the physisorbed to the chemisorbed state; k is Boltzmann' s constant; h is Planck' s constant; a and b are the ratios of the distribution functions of the transition complex and the adsorbed molecule, from which the zero energies have been separated out, for the transition from the physisorbed state into the gas phase and into the chemisorbed state, respectively. Solving this equation, we find the value of n_ϕ for the case $T \neq 0$

$$n_\phi = \frac{\chi_\phi \, dN/dt}{a e^{-q_\phi/kT} + b e^{-\varepsilon/kT}}. \qquad (3)$$

Fig. 1

The change in the concentration of chemisorbed molecules dn_x/dt will be

$$\frac{dn_x}{dt} = n_\phi b e^{-\varepsilon/kT} - n_x a_x e^{-q_x/kT}. \qquad (4)$$

Here q_x is the heat of chemisorption, and a_x is the same as a, but for desorption from the chemisorbed state; the second term on the right-hand side is equal to the flux of evaporating chemisorbed molecules.

Substituting (3) into (4), we find the condensation coefficient in chemisorption χ_x (evaporation is not taken into account)

$$\chi_x = \frac{d(n_x + n_\mathrm{i})}{dN} = \frac{\chi_\phi}{\dfrac{a}{b} e^{-(q_\phi - \varepsilon)/kT} + 1}, \tag{5}$$

and also the apparent condensation coefficient $\tilde{\chi}_x$ (evaporation is taken into account)

$$\tilde{\chi}_x = \frac{dn_x}{dN} = \frac{\chi_\phi}{\dfrac{a}{b} e^{-(q_\phi - \varepsilon)/kT} + 1} - \frac{n_x a_x e^{-q_x/kT}}{dN/dt}. \tag{6}$$

The second term on the right-hand side of (6) causes a decrease in $\tilde{\chi}_x$ with increasing n_x as a result of evaporation.

The apparent average condensation coefficient is equal to

$$\widetilde{K}_x = \frac{1}{n_x} \int_0^{n_x} \tilde{\chi}_x \, dn_x = \frac{\chi_\phi}{\dfrac{a}{b} e^{-(q_\phi - \varepsilon)/kT} + 1} - \frac{a_x}{n_x dN/dt} \int_0^{n_x} n_x e^{-q_x/kT}. \tag{7}$$

It follows from (5) that always $\varkappa_x \leqslant \varkappa_\phi$. In the case of physical adsorption of gases, q_ϕ is usually small. Therefore the Lennard-Jones theory of the condensation coefficient is applicable here (8), according to which $\varkappa_\phi < 1$ and is practically independent of temperature. For example, for the case of adsorption of hydrogen on metals, values lying in the range $0.16 \div 0.3$ were found in (8), which is in good agreement with experiment (3). Hence the independence of $\varkappa_x$ from temperature in the adsorption of oxygen on W over a wide temperature interval, which was found in the experiments of N. D. Morgulis and A. G. Naumovets (9), also becomes understandable, as well as in the adsorption of H_2 on W (see (3)) in that temperature interval where evaporation is not yet appreciable. In these cases $\varepsilon \simeq 0$, and $q_\phi \simeq 0.1 \div 0.2$ eV. It should be noted that the Lennard-Jones theory (8) does not take into account a possible dependence of $\varkappa_\phi$ on the concentration of adsorbed molecules, which may arise as a consequence of a change in the conditions of phonon exchange as the surface is filled. Expressions (6) and (7) describe the course of the dependences $\tilde{\varkappa}_x$ and $\widetilde{K}_x$ on n_x. Here it should be emphasized that q_x is a function of n_x, and q_x decreases strongly with increasing n_x owing to the interaction of adsorbed atoms or molecules (6). Therefore the magnitude of the second term in (6) and in (7) will depend very strongly on the value of q_x/kT, and consequently on n_x and on T.

Figure 1 gives the curves $\tilde{\varkappa}_x(n_x)$, calculated with the aid of (6) for the case of adsorption of hydrogen on W for three substrate temperatures: 1—310°K, 2—610°K, 3—740°K. The dependence $q_x(n_x)$ was taken from the work of O. Beeck $^{(10)}$. All these curves were calculated for three different values of dN/dt. For simplicity we put the value a_x equal to kT/h (where h is Planck' s constant). In the same figure the experimental data of Eisinger are given. The agreement of the calculated and experimental dependences $\tilde{\varkappa}_x(n_x)$ may be regarded as satisfactory. It should be noted that, with an increase of dN/dt or a decrease of the substrate temperature, the value of n_x at which $\tilde{\varkappa}_x$ begins to decrease will increase. At temperatures close to absolute zero, $\tilde{\varkappa}_x$ will be constant for any n_x.

The concepts developed here, moreover, agree at least qualitatively with Eisinger' s experimental data $^{(3)}$ on the course of the dependences $\tilde{\varkappa}_x(n_x)$ for the case of adsorption of N_2, O_2, and CO on W. For a quantitative comparison there are at present no data concerning the dependences $q_x(n_x)$.

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