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Abstract

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ON THE ADSORPTION ENERGY UPON IONIZATION OF ATOMS ON A METAL SURFACE

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In many problems connected with surface phenomena, knowledge of the adsorption energy is required. In our note a method is considered for finding this quantity and its dependence on the degree of coverage θ in the adsorption of alkali-metal vapors on a single-crystal metal surface.

Atoms adsorbed on the surface may desorb in the form of ions or in the form of neutral atoms. We assume that an atom, while on the metal surface, possesses a time-averaged charge $e_0 = ew$, where w is the ionization probability (the ratio of the number of desorbed ions to the number of incident atoms). Such a partially ionized adatom (adsorbed atom) will be called an adion. The charge of the adion and its electric image in the metal create a dipole with moment $\mu_0 = 2\delta e_0$, where δ is the distance from the center of the adion to the "reflecting plane." At a nonzero degree of coverage θ, the charge of the adion e' will differ from e_0. The layer of adions and their electric images forms a capacitor whose field acts on the charges of each dipole with a force $F = 4\pi {e'}^2\sigma$, directed opposite to the quasi-elastic force $F_0 = e_0^2/(2\delta)^2$ that held an isolated dipole in equilibrium (σ is the number of adatoms per unit surface). In this case the equality is satisfied

$$\frac{{e'}^2}{(2\delta)^2} = F_0 - F.$$

Hence

$$e' = \frac{e_0}{\sqrt{1 + 16\pi\delta^2\sigma}}. \tag{1}$$

The center of the negative charge of an adion need not coincide with the center of its positive charge. The distance between them $\delta_1(\theta)$ and δ, under certain assumptions, can be determined, for example, with the aid of the experimentally found dependence of the change in work function $\Delta\varphi = 2\pi\sigma\mu_\theta$ (^{1}) on θ. On the other hand, for $\Delta\varphi$ one may write the expression

$$\Delta\varphi = 4\pi\sigma e\delta - 4\pi\sigma(e - e')(\delta + \delta_1). \tag{2}$$

Then we have

$$\delta = \frac{\mu_\theta}{2e'} + \delta_1 \left(\frac{e}{e'} - 1\right). \tag{3}$$

From the slope of the tangent to the curve $\Delta\varphi(\theta)$ at $\theta = 0$, μ_0 is determined:

$$\mu_0 = \frac{\left.\dfrac{d\Delta\varphi}{d\theta}\right|_{\theta=0}}{2\pi\sigma_0} = \frac{\operatorname{tg}\alpha}{2\pi\sigma_0}, \tag{4}$$

where α is the angle between the tangent and the θ axis. Let us now assume that $\delta_1 = 0$ at $\theta = 0$, i.e., that the centers of the negative and positive charges of the adion coincide when it is alone on the surface. Then, putting $\theta = 0$ in (3) and substituting (4), we obtain

$$\delta = \frac{\operatorname{tg}\alpha}{4\pi e_0 \sigma_0}.$$

For δ_1, from (2) it follows that

$$\delta_1 = \frac{4\pi\sigma e'\delta - \Delta\varphi}{4\pi\sigma(e - e')}.$$

To clarify the dependence of the ion adsorption energy on θ, it is necessary to take into account the discrete structure of the layer of adatoms ([1]). Each adion together with its electric image constitutes a quadrupole with charges $-(e-e')$, e, $-e$, $(e-e')$ and distances between the charges δ_1, 2δ, δ_1, respectively (Fig. 1). On the crystalline surface of a metal, the adatoms form a plane lattice whose form is determined by the crystallographic structure of the surface. The distance between neighboring atoms is proportional to $\delta^{-1/2}$. From symmetry considerations it follows that the total force f acting on the ion from the layer of quadrupoles has only a component perpendicular to the surface. It is not difficult to obtain it by summing the perpendicular components of the interaction of the ion with each quadrupole. For adatoms with large r, summation may be replaced by integration.

Fig. 1

Taking into account that the adsorption energy of the ion is equal to $\lambda_+ = -\int_\delta^\infty f\,dx$, we can obtain

$$-\lambda_+ = -\frac{e^2}{4\delta} + U_1 + U_2 + U_3,$$

where the first term is the energy of interaction of the ion with its electric image, U_1 is the energy due to the electrostatic interaction with adions close to the point $x = 0$, i.e., a certain sum over r of terms of the form

$$U_r = e^2\left(\frac{1}{r} - \frac{1}{\sqrt{r^2 + 4\delta^2}}\right) - e(e - e')\left(\frac{1}{\sqrt{r^2 + \delta_1^2}} - \frac{1}{\sqrt{r^2 + (2\delta + \delta_1)^2}}\right),$$

U_2 is the energy of interaction with distant adions, equal to

$$U_2 = 2\pi\sigma e^2\left(\sqrt{R^2 + 4\delta^2} - R - 2\delta\right) -$$

$$-2\pi\sigma e(e - e')\left(\sqrt{R^2 + (2\delta + \delta_1)^2} - \sqrt{R^2 + \delta_1^2} - 2\delta - 2\delta_1\right),$$

where R is that value of r starting from which summation is replaced by integration, and U_3 includes the energy of nonelectrostatic origin. A calculation carried out for a specific system—cesium on the (110) face of tungsten (^{2})—gave for λ_+ the dependence shown in Fig. 2 by curve 1. In doing so it was assumed that U_3 does not depend on θ, i.e.,

$$\lambda_+ = \lambda_+^0 + \lambda_+^0(\theta),$$

where

$$\lambda_+' = U_1 + U_2.$$

Curve 2 represents the experimentally found dependence $\lambda_+(\theta)$ (^{2}).

Fig. 2

If the ionization potential of the atoms V is less than the work function of the adsorbent φ, then the curve of the dependence of the ionic-current density I on the temperature T exhibits a characteristic threshold point, whose existence is

ciated—

is associated with a decrease in the work function φ by adatoms.* I is determined by the formula (^{3,4})

$$n^+ = \frac{\sigma}{\tau_0} g_2 \exp\left(-\frac{\lambda_+}{kT}\right), \tag{5}$$

where n^+ is the ion flux density, g_i is the statistical weight of the ion, and τ_0 is a quantity only weakly dependent on temperature. For not very large θ, the quantity $\delta_1(\theta)$ may be neglected. Then, from the parameters of three threshold points, one can determine δ and, consequently, $\lambda_+(\theta)$ for not very large θ. We choose three threshold temperatures so that

$$\frac{1}{T_1} - \frac{1}{T_2} = \frac{1}{T_2} - \frac{1}{T_3}$$

and take the ratio n_1^+/n_2^+ to n_2^+/n_3^+. With the aid of (5) we obtain:

$$\frac{n_1^+ n_3^+}{(n_2^+)^2} = \frac{\sigma_1 \sigma_3}{\sigma_2^2} \exp\left[\frac{1}{k}\left(\frac{2\lambda'_{+2}}{T_2} - \frac{\lambda'_{+1}}{T_1} - \frac{\lambda'_{+3}}{T_3}\right)\right]. \tag{6}$$

Taking into account the smallness of θ at the threshold point, we have for σ and λ'_+ on the (001) face of tungsten

$$\sigma_1 = \frac{\Delta\varphi_1}{4\pi e_{01}\delta}\left(1 + \frac{2\Delta\varphi_1\delta}{e_{01}}\right), \tag{7}$$

$$\lambda'_+ = \Delta\varphi e\left(1 - \frac{4.315}{\pi}\sqrt{\frac{\Delta\varphi\delta}{4\pi e_0}}\right). \tag{8}$$

The quantities $\Delta\varphi$ and e_0 are determined from the experimental data using the Saha-Langmuir equation. Thus, from (6), (7), and (8) one can find δ. From the ratio n_1^+/n_2^+ we find λ_+^0, and from (5) the value τ_0. Knowing the dependence of λ_+ and $\lambda_0 = \lambda_+ + (\varphi - V - \Delta\varphi)e$ on θ, and using, to find θ, the stationarity condition

$$n = \frac{\sigma}{\tau_0}\left[g_i \exp\left(-\frac{\lambda_+}{kT}\right) + g_a \exp\left(-\frac{\lambda_0}{kT}\right)\right], \tag{9}$$

where n is the flux density of atoms incident on the surface, we can reconstruct the dependence $I(T)$, calculate threshold points in any region of n and T. The known empirical extrapolation relations connecting the current and the temperature at the threshold points (5–7), as well as the evaporator temperature T with the threshold temperature of the emitter T (5,8), can be substantiated (9) and refined. Using the ratio n_1^+/n_2^+ and, in the first approximation, (7) and (8), we find:

$$\lg\frac{I}{I_1} = -\frac{5040}{T}\lambda_+ + \frac{5040}{T_1}\lambda_{+1} + \lg\left(\frac{\Delta\varphi}{\Delta\varphi_1}\frac{w_1}{w}\right). \tag{10}$$

Fig. 3

* The change in the work function caused by the field drawing off the ions is taken into account, as usual (^{9}), by the effective value of φ.

Noting that the flux density of particles from the evaporator n is determined by an equation similar to (5), we obtain for the stationary case

$$T = \frac{\lambda_+ T}{\lambda + kT \ln \frac{\sigma g_i}{C\tau_0\beta}}, \tag{11}$$

where λ is the heat of evaporation of the ionizing substance, β is the ionization coefficient, and C is a quantity weakly dependent on temperature (a pre-exponential factor analogous to $\sigma g_i/\tau_0$).

Measurements of ionic currents during the adsorption of potassium on the (001) face of tungsten were carried out with the aid of a dismountable apparatus, whose emitter and collector were made of tungsten and tantalum ribbon, respectively. The temperature of the emitter was measured with a thin high-temperature tungsten-rhenium thermocouple $^{(10)}$. The pressure of potassium vapor in the volume of the apparatus was determined from the temperature of the potassium in the evaporator using empirical tables and formulas $^{(11)}$. The emitter was made of rolled tungsten 0.2 mm thick. As a result of rolling, the tungsten was strongly textured. X-ray structural studies carried out on a URS-50I installation equipped with an attachment for texture studies showed that the surface of the emitter consisted practically entirely of (001) plane exits and, as a result, was homogeneous with respect to the work function.

Our experiments (Fig. 3) led to values of the saturation ionic currents I, the corresponding threshold temperatures T, and ionization coefficients β (ω is the ionization coefficient (ionization probability) on a clean surface). The data obtained made it possible to perform all the necessary calculations. In doing so, the ionization potential of potassium and the electron work function from the (001) face of tungsten were taken to be 4.34 V and 4.52 eV, respectively. The value found for λ_+^0 was about 2.2 eV. The curve $\Delta\varphi(T)$ (Fig. 3), constructed from the experimental data, can be represented with a high degree of accuracy by the equation

$$\Delta\varphi\,(V) = 1.2 \cdot 10^{-2084/T} \tag{12}$$

and for our temperature interval, from (10), we obtain

$$T = \frac{13600}{8 - \lg I}.$$

Here I is expressed in $\mathrm{A} \cdot \mathrm{cm}^{-2}$. For higher temperatures, the change of λ_+' with T according to formula (12) should be taken into account. Taking the heat of evaporation of potassium λ equal to 0.88 eV $^{(11)}$, according to (11) we have

$$T = 3.3T\,,$$

which is sufficiently close to the data of work (8).

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