PHYSICAL CHEMISTRY

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1964

SovietRxiv

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Abstract

Full Text

PHYSICAL CHEMISTRY

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DEPENDENCE OF HYDROGEN CHEMISORPTION AT THE METAL–SOLUTION INTERFACE ON THE pH OF THE SOLUTION

(Presented by Academician A. N. Frumkin, 16 V 1964)

The change in the bond energy and in the amount of hydrogen adsorbed at the metal—solution interface with change in the pH of the solution is a widespread regularity ($^{1-8}$). However, the form of the functional relationship of these quantities with pH has not been established. In order to obtain such data, at room temperature we recorded charge curves of a rhodized platinum electrode in $1.0 \cdot 10^{-3}$: 1.0 N sulfuric acid solutions at a constant concentration of sulfate ion of 1 g-equiv/liter*.

With increasing pH, the following changes are observed in the charge curves of rhodium and rhodium powder (^{5}): the double-layer region decreases, the polarization double-layer capacitance of the electrode increases somewhat, and the hydrogen region of the curves broadens.

The hydrogen portions of the curves and the adjacent double-layer portions practically coincide when superposed on the curve obtained at pH 0.55 without rotating the coordinate axes (Fig. 1). In such a construction the coinciding points of the charge curves correspond, to a first approximation, to identical values of θ, the degree of filling of the rhodium surface with adsorbed hydrogen.

Fig. 1. Superposition of charge curves of compact rhodium, recorded at pH 0.55 (1); 1.70 (2); 2.86 (3); 4.00 (4). I —coordinates for curve 1, IV —for curve 4. The coordinates for curves 2 and 3 lie between these limiting pairs of coordinates.

Fig. 2. Dependence of $\varphi_r - \varphi_0$ on pH for compact (a) and dispersed (b) Rh. The latter was constructed from data of (5).

Figure 2: Fig. 2. Dependence of $\varphi_r - \varphi_0$ on pH for compact (a) and dispersed (b) Rh. The latter was constructed from data of (5).

a –tangent to the curves in the double-layer region

As can be seen from Fig. 2, the ordinates φ_r and φ_0 in Fig. 1 for any coincident points of the curves are connected by a linear relation

* Previously, charge curves of rhodized platinum black powder were recorded in analogous solutions (^{5}).

$$\varphi_r = \varphi_0 + \frac{2.303RT}{2F} Z\,(\mathrm{pH} - \mathrm{pH}_0), \tag{1}$$

where φ_0 and pH_0 refer to the solution chosen as the standard one, Z is a constant, and the remaining notation is conventional. In Figs. 1 and 2, φ_0 corresponds to $\mathrm{pH}_0 = 0.55$. Both for compact and for dispersed rhodium, $Z = 0.52$.

Obviously, in accordance with (1), for any value of θ the following holds:

$$\ln \frac{p_r}{a_r^Z} = \ln \frac{p_0}{a_0^Z} = \ln \sigma, \tag{2}$$

where a is the activity of the hydronium ion and σ is a function of θ. Thus, under isothermal conditions in the presence of electrolyte, θ is determined by the parameter $\sigma = p/a^Z$, and not by p.

Figure 3 gives data on the adsorption of hydrogen on rhodium as a function of $\sigma = p/a^{0.52}$. In constructing these isotherms, the consumption of electricity for charging the double layer was approximately allowed for by linear extrapolation of the double-layer portion of the charging curve into the region of more negative potentials (Fig. 1, straight line a). At $\sigma \approx 10^{-3}$, a break is observed in the isotherms. For $\sigma < 10^{-3}$, the isotherm is described by the equation:

$$A = (A_0\sigma)^{0.39}, \tag{3}$$

and for $\sigma > 10^{-3}$ by the equation

$$A = A_0' + B\lg\sigma. \tag{4}$$

Fig. 2. Dependence of $\varphi_r - \varphi_0$ on pH for compact (*a*) and dispersed (*b*) Rh. The latter was constructed from data of (5).

The values of the constants A_0, A_0', and B are given in Table 1. These equations are analogous to the Freundlich and Temkin equations, respectively; however, here A is a function of σ, and not of p. A denotes hydrogen adsorption in C/cm^2 (compact rhodium) or C/g (rhodium black).

Table 1

Constants	A_0	A_0'	B
Rh electrode	13.8	0.294	0.029
Rh black	$21.4 \cdot 10^6$	71.2	8.10

The fact that hydrogen adsorption on an electrode under the conditions of a reversible hydrogen electrode must depend on σ follows from more general considerations.

For a platinized platinum electrode operating under the indicated conditions, A. N. Frumkin and A. I. Shlygin (^{1}), from the Gibbs adsorption equation, obtained the relation:

$$\frac{(\partial A/\partial \mu_{H+})_{\mu_H}}{(\partial A/\partial \mu_{H+})_{\mu_H} + (\partial A/\partial \mu_H)_{\mu_{H+}}} = \left(\frac{\partial E}{\partial A}\right)_{\varphi} = -\frac{(\partial \varphi/\partial A)_E}{(\partial \varphi/\partial E)_A}; \tag{5}$$

where

$$\mu_H = \mu_H^0 + RT \ln p_H = \frac{1}{2}\left(\mu_{H_2}^0 + RT \ln p\right); \tag{6}$$

$$\mu_{H+} = \mu_{H+}^0 + RT \ln a; \tag{7}$$

A is the adsorption of hydrogen (C/cm^2); E is the density of electric charge on the electrode surface (C/cm^2); φ is the electrode potential; p and p_H are partial pressures of molecular and atomic hydrogen, respectively; μ_H^0, $\mu_{H_2}^0$, and $\mu_{H^+}^0$ are constants.

Equation (5) is satisfied in acid and salt solutions under the condition that the anion concentration is constant and the H$^+$ ion does not participate in the formation of the ionic double layer, i.e., when the solution contains either an excess of another cation, for example Na$^+$, or the surface is positively charged. Transforming (5), taking into account (6) and (7), and the equation $\theta = CA$, where C is a constant,

$$\left(\frac{\partial \theta}{\partial \ln a}\right)_p = -K \left(\frac{\partial \theta}{\partial \ln p}\right)_a, \tag{8}$$

Fig. 3. Dependence of A on σ = P/a^0.52 for dispersed (1) and compact (2) Rh. The ordinates of curve 2 are shifted upward by 3 units. The point symbols correspond to the following pH: a –0.55; b –0.95; v –1.70; g –1.86; d –2.04; e –2.24; zh –2.55; z –2.86; i –3.25; k –4.00

Figure 3: Fig. 3. Dependence of A on σ = P/a^0.52 for dispersed (1) and compact (2) Rh. The ordinates of curve 2 are shifted upward by 3 units. The point symbols correspond to the following pH: a –0.55; b –0.95; v –1.70; g –1.86; d –2.04; e –2.24; zh –2.55; z –2.86; i –3.25; k –4.00

where

$$K = \frac{2(\partial\varphi/\partial A)_E}{(\partial\varphi/\partial A)_E + (\partial\varphi/\partial E)_A} = \frac{2(\partial E/\partial A)_\varphi}{(\partial E/\partial A)_\varphi - 1}. \tag{9}$$

Let, at a given pH and constant temperature, the adsorption of hydrogen on the metal be described by the Langmuir equation

$$\theta = \frac{\sqrt{bp\exp(q^0/RT)}}{1 + \sqrt{bp\exp(q^0/RT)}}, \tag{10}$$

where b is the adsorption coefficient, q^0 is the differential heat of adsorption at standard pH (a constant independent of either p or a ([9,10])).

Fig. 3. Dependence of A on $\sigma = P/a^{0.52}$ for dispersed (1) and compact (2) Rh. The ordinates of curve 2 are shifted upward by 3 units. The point symbols correspond to the following pH: *a* –0.55; *b* –0.95; *v* –1.70; *g* –1.86; *d* –2.04; *e* –2.24; *zh* –2.55; *z* –2.86; *i* –3.25; *k* –4.00.

After differentiating (10) with respect to the variables a and p, at constant p and a, respectively, and substituting the results into (8), we obtain

$$\frac{d\ln b}{d\ln a} = -K. \tag{11}$$

The same result is obtained for the case of the Freundlich and Temkin isotherms. In the differentiation it was assumed that b depends on a and does not depend on p. Let us take

$$b = b_0\exp(\Delta q/RT), \tag{12}$$

where b_0 is the adsorption coefficient in the standard solution, and Δq is the change in the differential heat of adsorption upon going from the given solution to the standard one. Obviously, in accordance with what was said above, Δq depends on the pH of the solution and does not depend on p or θ.

We have chosen as the standard a solution with pH 0. Integrating (11), taking (12) into account, over the limits from a to $a = 1$, under the assumption that K does not depend on a, gives:

$$\Delta q = -RTK \ln a = 2.303 RTK \,\text{pH}. \tag{13}$$

After transforming the Langmuir, Freundlich, and Temkin equations (for mean values of θ), taking (12) and (13) into account, we obtain, respectively:

$$\Theta = \frac{\sqrt{b_0 \sigma' \exp(q^0/RT)}}{1 + \sqrt{b_0 \sigma' \exp(q^0/RT)}}; \tag{14}$$

$$\theta = (b_0 \sigma')^n; \tag{15}$$

$$\theta = \theta_0 + m \ln \sigma'. \tag{16}$$

Here m, n, q^0, θ_0 are constants and $\sigma' = p/a^k$.

It is not difficult to see that the equations obtained for rhodium from the experimental data, equations (3) and (4), are identical to equations (15) and (16), respectively. It is interesting that equations of the type (15) and (16) describe the dependence of θ on σ' also in cases where no foreign cation is present in the solution (pH 0.55). Possibly, in the range of potentials studied, the surface of rhodium is positively charged*.

It can also be shown that a dependence of type (13) follows from the data obtained in the present work on the adsorption of hydrogen on rhodium. Indeed, differentiating (2) with respect to T at constant θ and taking into account that, first,[9]

$$q = RT \left[1 + T \left(\frac{\partial \ln p}{\partial T} \right)_\theta \right],$$

where q is the differential heat of adsorption; secondly,

$$\frac{d}{dT} \left(\ln \frac{a_1}{a_2} \right) = 0$$

by virtue of the constancy of the ionic strength of the solutions, we obtain:

$$q = q_0 + RT^2 \frac{dZ}{dT} \ln a = q_0 - 2.303 RT^2 \frac{dZ}{dT} \,\text{pH}. \tag{17}$$

In equation (17), q_0 is the differential heat of adsorption of hydrogen at $a = 1$, and $RT^2 \dfrac{dZ}{dT} \ln a = \Delta q$ is the change in the heat of adsorption in passing from the standard solution to the given solution. The constants $Z = T\, dZ/dT = K$ may be equated to one another on dimensional grounds.

Thus, adsorption of hydrogen at the metal–solution interface is a function of the ratio $\sigma = P/a^k$, where the magnitude K is determined by equation (9). The sign and magnitude of K are determined by the sign of $(\partial\varphi/\partial A)_E$, since $(\partial\varphi/\partial E)_A > 0$ by definition, and $|(\partial\varphi/\partial E)_A| \geq (\partial\varphi/\partial A)_E$, because the contribution of the adsorbed ion $(\partial\varphi/\partial E)_A$ to the potential jump at the electrode –solution interface cannot be smaller than $(\partial\varphi/\partial A)_E$, the contribution of the adsorbed hydrogen atom. Obviously, $0 \leq K \leq 1$ when $(\partial\varphi/\partial A)_E > 0$, and $-\infty < K < \infty$ when $(\partial\varphi/\partial A)_E < 0$. Thus, in principle, according to equations (13), (15), (16), Δq and θ may either increase or decrease with increasing a.

For rhodium, K and $(\partial\varphi/\partial A)_E$ are positive; hence the polar bond rhodium–hydrogen is oriented with its negative end toward the solution.

For platinized platinum, θ also depends on pH; however, it has not been possible to treat the results in an analogous way.

We consider it a pleasant duty to express our gratitude to Academician A. N. Frumkin for valuable advice in discussing the results of the work.

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Received
15 V 1964

CITED LITERATURE

1. A. N. Frumkin, A. I. Shlygin, *Izv. AN SSSR, OKhN*, 1936, No. 5, 773.
2. A. F. Lunev, Candidate' s dissertation, Moscow, 1948.
3. A. D. Obrucheva, I. L. Rubinshtein, *DAN*, **63**, 403 (1948).
4. V. A. Past, Candidate' s dissertation, Moscow, 1956.
5. Yu. M. Tyurin, *DAN*, **126**, 827 (1959).
6. T. M. Grishina, G. I. Khomchenko, G. D. Vovchenko, *Vestn. MGU*, Ser. 2, Khim., **2**, 53 (1962).
7. V. Böld, M. W. Breiter, *Zs. Elektrochem.*, **64**, 897 (1960).

8. Yu. A. Skopin, D. V. Sokol' skii, *Proceedings of the First Interuniversity Conference on Catalysis*, Moscow, 1962, p. 486.

9. V. Trepnel, *Chemisorption*, IL, 1958, Chs. 3–7.

10. G. M. Panchenkov, V. P. Lebedev, *Chemical Kinetics and Catalysis*, 1961, p. 370.

* This assumption requires further study.

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

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