THE MECHANISM OF THE VERTICAL DISTRIBUTION OF $\mathrm{H_2O_2}$ ABOVE A SOLUTION

1958

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

I. L. ROIK and I. P. BOLOTICH

THE MECHANISM OF THE VERTICAL DISTRIBUTION OF H_2O_2 ABOVE A SOLUTION

(Presented by Academician A. N. Frumkin, 2 I 1958)

In work ([1]) it was established that photographically active particles emitted from the surface of metals during atmospheric corrosion decrease with distance according to an exponential law. Since the indicated particles are molecules of H_2O_2 ([2–4]), one could expect that there also exists a vertical distribution for hydrogen peroxide vapor emitted from a solution. To confirm this circumstance, the following experiments were carried out.

An aqueous solution of hydrogen peroxide of a definite concentration was poured into a cuvette, and a photographic plate was placed at a small angle to the surface of the solution. The experimental conditions were as follows. Photographic plates: Isoorto, emulsion No. 747, exposure 5 min.; heating of the photographic plate after exposure in a thermostat ([5]) for 10 min. at a temperature of 100°; development time 3 min. at 20°; relative humidity of the air in the laboratory room 62%, ambient temperature 20°.

As a result of the experiments, a linear dependence was established between the blackening D and its height h above the surface of the hydrogen peroxide solution:

$$D = -bh + A,. \tag{1}$$

where b and A are constants.

The curves in Fig. 1 were obtained as a result of averaging the data of 10 experiments at constant exposure.

The aim of the subsequent investigation was to elucidate the mechanism of the vertical distribution of H_2O_2 evaporating from a solution. If one assumes that H_2O_2 molecules decompose on dust particles in the air, then the decrease in the number of hydrogen peroxide molecules in a volume dv must be proportional to the initial number of molecules n in this volume and to the number of dust particles N_p causing decomposition:

$$-dn = knN_p.$$

Since

$$N_p = n_p\, dv = n_p\, s\, dh,$$

(where n_p is the number of dust particles causing decomposition per unit volume), then

$$-dn = kn\, n_p\, s\, dh.$$

Hence

$$-\ln n = kn_{psh} + C$$

at $h = 0$, $n = n_0$, and $C = -\ln n_0$.

Then

$$n = n_0 e^{-kn_{psh}}. \tag{2}$$

Equation (2) shows that the number of hydrogen peroxide molecules decreases exponentially with height above the solution. The equation of the characteristic

of the photolayer curve for the linear section, when the reciprocity law (6), which in the present case is justified, is fulfilled, has the form

$$D = \gamma(\ln Et - \ln E_i t_i). \tag{3}$$

In work (7) it was shown that there is a direct proportional dependence between the number of H_2O_2 particles released from the solution and the number of particles striking the photolayer. On this basis one may assume that $E = k'n$. Then

$$D = \gamma(\ln k' n_0 e^{-kn_p sh} t - \ln k' n_i t_i),$$

$$D = \gamma(\ln k' n_0 t - \ln k' n_i t_i - kn_p sh).$$

Let us denote

$$A = \gamma \ln \frac{n_0 t}{n_i t_i}; \qquad b' = \gamma ks.$$

Then we obtain

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

$$D = -b' n_p h + A, \tag{4}$$

i.e., an equation analogous to (1), obtained experimentally. It follows from equation (4) that the angle of inclination of the straight line depends on the number of dust particles (n_p). As the number of dust particles causing decomposition of H_2O_2 decreases, the angle of inclination of this straight line to the abscissa axis increases.

Fig. 1. Dependence of the blackening of the photolayer on its height above the surface of the H_2O_2 solution for different concentrations of the latter

Fig. 2. Dependence of the blackening of the photolayer on its height above the surface of the H_2O_2 solution. I—in dusty air, II—in partially dust-free air

For an experimental verification of formula (4), the dependence of D on h was established in dusty and partially dust-free air above the surface of an H_2O_2 solution. Iso-orthochromatic photographic plates were used, with light sensitivity according to GOST 32, emulsion No. 3, exposure 4 min. For partial dust removal from the air, the air pumped by a pump was purified by an electrofilter and fed into the vessel where the photographic plates and the hydrogen peroxide solution were placed. The exposure was made after purification of the air in the vessel. The electrofilter was a metal cylinder along the axis of which a wire was stretched, to which the negative pole of an induction coil was connected; the cylinder was grounded. The electrofilter operated in the corona-discharge region. In order to avoid blackening of the photographic plate under the action of ozone formed in the electrofilter, the purified air, before entering the vessel, was passed through a heater, in which the ozone

underwent dissociation. The results presented in Fig. 2 are averages from 5 experiments. The values of the optical density of straight lines *I* and *II* lie within the range of the photometric interval, which was established by plotting the characteristic curve. In accordance with formula (4), straight line *II*, obtained in partially dust-free air, is flatter than *I*, recorded in the presence of dust in the air above the surface of the H_2O_2 solution.

Thus, the experimental data obtained indicate that the decrease with height of hydrogen peroxide molecules evaporating from the solution is associated with the presence of dust particles in the air.

We consider it our pleasant duty to express our gratitude to Academician A. N. Frumkin, who pointed out to us the possibility of explaining the vertical distribution of H_2O_2 by the decomposition of peroxide on dust particles.

Odessa Technological Institute
named after I. V. Stalin

Received
21 XI 1957

CITED LITERATURE

1. I. L. Roikh, DAN, **70**, No. 2, 253 (1950).
2. I. L. Roikh, D. M. Rafalovich, DAN, **60**, No. 4, 603 (1953).
3. I. L. Roikh, DAN, **64**, No. 6, 1117 (1954).
4. I. L. Roikh, DAN, **108**, No. 6, 1102 (1956).
5. I. L. Roikh, ZhFKh, **30**, issue 4, 954 (1956).
6. I. L. Roikh, D. M. Rafalovich, *Ukr. Khim. Zhurn.*, **24**, No. 2, 198 (1958).
7. I. L. Roikh, ZhFKh, **31**, No. 9, 1959 (1957).

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