

Concentration-dependent diffusivity: Hydrogen percolation in WO_3

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The diffusivity of H in a thin layer of WO_3 was measured optically through the visible optical absorption of the H-containing substance. Microdensitometry and the photoresist technique made a $1\text{-}\mu\text{m}$ lateral resolution available. When the data were evaluated by Boltzmann's method, the diffusion coefficient, as low as about $D_m \approx 10^{-11} \text{ cm}^2/\text{sec}$ at high H concentrations, was shown to increase sharply with decreasing H content. This behavior was quantitatively understood in terms of a percolation model modified by assuming H atoms to jam fast channels. The extreme low-concentration diffusion coefficient D_0 was evaluated by virtue of this model and gave $D_0 \approx 10^{-9} \text{ cm}^2/\text{sec}$.

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I. INTRODUCTION

The electrochromatic effect of WO_3 in contact with aqueous solutions seems to be a process of importance in practice (in view of its potential application in display systems), and intriguing as far as its basic understanding is concerned. In this paper, we focus our attention on the second of these aspects.

The electrochromatic effect, i.e., the change of color due to an external electric field, can be brought about if a thin, transparent, and colorless layer of WO_3 is immersed in an aqueous solution and a cathodic bias is applied. This turns the layer blue, a change which remains after the termination of the current flow. The coloration deepens with increasing negative potential of the layer; at a given potential and after some time, the current vanishes and optical absorption becomes constant.

Investigating the NMR spectrum of WO_3 in contact with nascent hydrogen Nishimura¹ has shown that hydrogen atoms are present in the lattice. WO_3 crystals are known to have a structure in which two types of channels are formed, both of which are perpendicular to the (001) plane. In analogy to the structure of alkali W bronzes,² H atoms are thought to be located in one or both types of channels. This statement does not necessarily mean that H atoms directly cause optical absorption; this is usually ascribed to a reduced valency W ion.³ There is no doubt, however, that the blue phase is characterized by the composition H_xWO_3 —with the equilibrium value of x being governed by the external voltage.

Electrochemical investigation of electrochromatic kinetics suggests that the diffusivity of H in the solid phase greatly influences the rate of the electrochromatic process. Reichman, Bard, and Laser,⁴ by studying the kinetics of coloration in great detail, found the H diffusion coefficient by parameter fitting to be $D_H = 1 \times 10^{-9} - 2 \times 10^{-10} \text{ cm}^2/\text{sec}$. Hitchman⁵ observed an average $D_H = 1.4 \times 10^{-11} \text{ cm}^2/\text{sec}$ by chronoamperometry, if the solid phase composition was $0.0012 < x < 0.071$. Another estimate based on NMR measurements of ill-defined samples² resulted in an extrapolated value of $D_H = 10^{-9} \text{ cm}^2/\text{sec}$. The kinetics of bleaching could be understood in terms of space-charge-limited transport of the solid-state $\text{H}^+ + e^-$ plasma.⁶

The aim of the present study was to measure and to try to interpret the diffusivity of H in WO_3 layers. To this end, thin layers of WO_3 were investigated optically. Part of the layer was homogeneously saturated with H, and the diffusion parallel to the layer surface was measured by detecting the spread of the optical absorption. The boundary line between the H-containing and the virgin parts of the layer was prepared in such a way that the initial H concentration profile at the boundary could be approximated reasonably well by a step function. The measurements were made by a microdensitometer; the data were evaluated by Boltzmann's method, which could account for an eventual concentration dependence of the diffusion coefficient. For a quantitative description of the observations, a modified percolation model is proposed.

II. EXPERIMENTAL

A. Sample preparation

Transparent WO_3 layers of $0.5\text{-}\mu\text{m}$ thickness were vacuum deposited on glass plates covered with indium-tin oxide.

The extinction coefficient of H_xWO_3 was known to be $\epsilon = 4.56 \times 10^6 \text{ cm}^2/\text{mol}$ at the 650-nm wavelength⁷; we used this value as a standard for the spectrophotometric determination of ϵ at other wavelengths.

Knowing the earlier estimates for D_H cited in Sec. I and considering the relationship $\langle z^2 \rangle = 2Dt$, an approximate $10\text{-}\mu\text{m}$ spread of the concentration profile was expected to take place during the course of several hours. Hence, practical arguments compelled us to make an initial concentration edge of a shape which can be taken as an ideal step function within an accuracy of $1\text{-}\mu\text{m}$. For that purpose, $1\text{-}\mu\text{m}$ -resolution photolithography was used. The result was a WO_3 layer partly covered by an insulating film, which prevented H atoms from entering the oxide. The film edge was observed to be a rectangular step on the $1\text{-}\mu\text{m}$ scale of a Talystep instrument. A schematic picture of the structure is given in Fig. 1.

This structure was immersed in sulfuric acid, and the unprotected part of the WO_3 layer was saturated with H. This was effected electrolytically in $0.1 \text{ N H}_2\text{SO}_4$ solution under potentiostatic conditions. Electrolysis was carried out

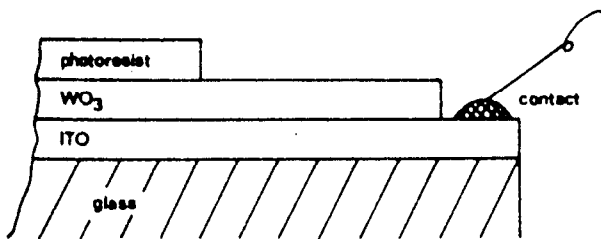


FIG. 1. Schematic picture of the sample. ITO = indium-tin oxide.

until the current virtually vanished, thus ensuring uniform H concentration with depth. The potential of the WO_3 electrode was adjusted between 0.096 and 0.046 V versus a normal hydrogen electrode (NHE). Here the saturation concentrations were low enough to satisfy Lambert-Beer's law.⁷

B. Microdensitometry

The lateral distribution of optical absorption was measured by a 1- μm resolution power microdensitometer based on an Amplival microscope (Carl Zeiss, Jena). The intensity distribution on the screen was measured by a low-noise photodiode whose position perpendicular to the image of the H step was adjustable, thereby providing a positioning better than the resolution of the optical setup. The analyzing light intensity was kept as low as possible to avoid both photochromatic effect and thermal decomposition.⁸ The analyzing wavelength, selected by an interference filter, was 680 nm.

The stability of H_xWO_3 was checked optically by independent measurements; the compound was seen to have a half-life longer than 5×10^5 sec, which compared favorably with the average duration of a run, i.e., some 2×10^4 sec.

The resolution of the microdensitometer defined the lower boundary of the displacement that could be measured. The intensity distribution of the incoherent picture of an ideal edge is given⁹ as

$$I(z)/I(\infty) = 0.5 + \text{Si}(az)/\pi - [1 - \cos(az)]/\pi az, \quad (1)$$

where z is the distance perpendicular to the image of the edge; $I(z)$ and $I(\infty)$ are intensities at z and far from the edge, respectively; a is a value characteristic to the resolution power; and Si symbolizes the integral sin function. Using a black edge, we found $a = 2.0 \mu\text{m}^{-1}$ by Eq. (1); a^{-1} being about equal to the half-width of the transmission function.

Thus the first diffusivity measurement needed to be carried out when the spread of the H edge due to diffusion was considerably larger than a^{-1} , the optical spread of the image. Experience taught us that this condition was met after one hour.

The measurement consisted in the determination of the time-dependent light intensity profiles $I(z,t)$ which, by knowing the layer thickness and extinction coefficient and by using Lambert-Beer's law, enabled us to evaluate the time-dependent concentration distribution $c(z,t)$.

C. Data treatment

Even the first inspection of the apparently asymmetric $c(z)$ profiles pointed to an eventual concentration depen-

dence of the diffusion coefficient. Thus the use of Boltzmann's method¹⁰ seemed to be advisable. The general one-dimensional diffusion equation is of the form

$$\frac{\partial c(z,t)}{\partial t} = \frac{\partial}{\partial z} \left[D(c) \frac{\partial c(z,t)}{\partial z} \right], \quad (2)$$

which can be transformed into an ordinary differential equation

$$\frac{d}{dy} \left[D(c) \frac{dc}{dy} \right] = -\frac{y}{2} \frac{dc}{dy} \quad (3)$$

using the new variable $y = zt^{-1/2}$. This can be done only if the initial concentration distribution is a step function. Integrating Eq. (3) between actual concentration c and initial concentration c_0 , one obtains $D(c)$ as

$$D(c) = \frac{1}{2} \frac{dy}{dc} \int_c^{c_0} y dc. \quad (4)$$

We treated our measurements numerically in terms of Eq. (4). The exact position of the origin, $z = 0$, was to be determined independently. This was based on early $c(z,t)$ data, where t was so small as to make diffusion practically negligible.

In order to test the numerical process, an analytically exact solution of Eq. (2) was perturbed with an artificial random error, and the figures produced in that way were used as $c(y)$ input data. The exact solution was

$$c(y) = c_0 [1 + \text{erf}(y/2D^{1/2})]/2, \quad (5)$$

which refers to the $D(c) = D = \text{constant}$ case, and a random generator was applied as a source of error. The expectation was that a concentration-independent D would be recovered as a result of the numerical process, which was indeed the case, even if there was an 8% relative error of the input data.

III. RESULTS

The $c(z,t)$ data observed are given in Fig. 2. The diffusivity of H in WO_3 , as evaluated by Eq. (4) was found to vary greatly with H content. The concentration interval studied was $0 < c < 3 \times 10^{-3}$ mol/cm³; the initial concentrations, c_0 , varying between 2.5×10^{-3} mol/cm³ and 4.0×10^{-3} mol/cm³. The concentration data were expressed in terms of the variable x of the formula H_xWO_3 , the relationship being $x = 32.4c$.

$D(c)$ was found to be independent of c_0 . The rapid increase of D with decreasing x strongly suggested that our highest D value observed was not the upper limit. As far as the smoothness of the $D(c)$ curves was concerned, the error limit of one run was reasonable, whereas the reproducibility of subsequent runs, which involved either different portions of the same sample or even different samples, was rather poor. This we are inclined to attribute mainly to the inhomogeneity or the local faults of the WO_3 layers. Hence Fig. 3 presents the results of one single run only, where $I(z,t)$ was measured at 15 points at four different moments. For detailed error analysis, see Sec. IVB.

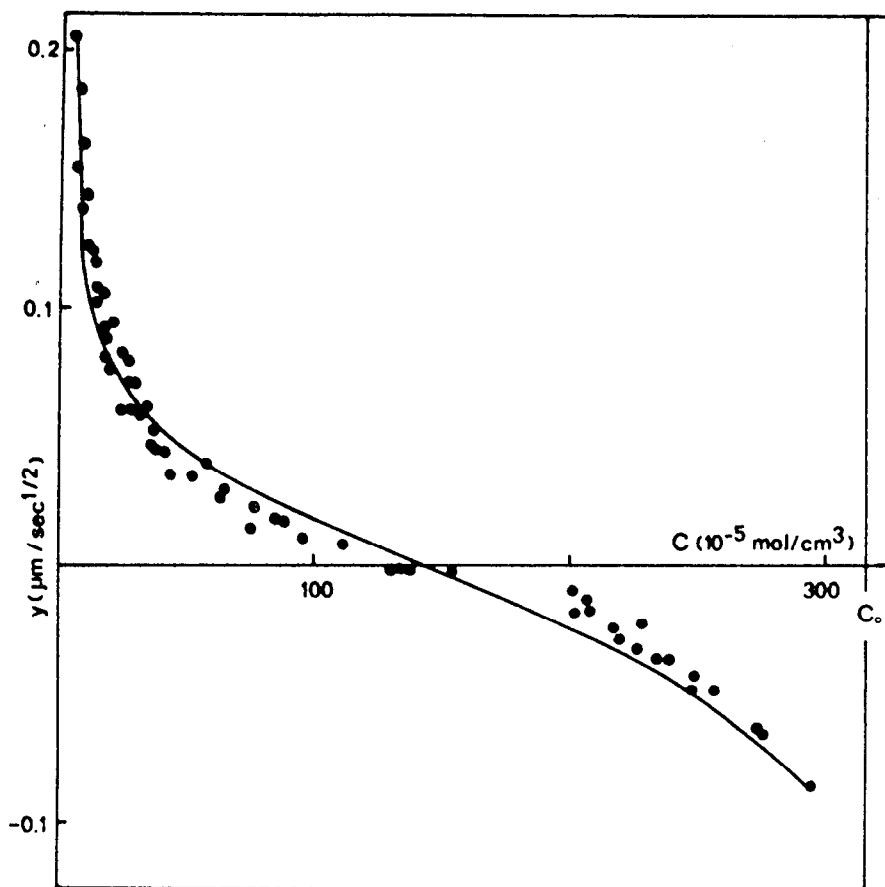


FIG. 2. Concentration profiles after Boltzmann transformation $c(y)$. ●: measured. Solid curve: curve smoothed numerically.

The highest D value observed was $D(x = 5 \times 10^{-3}) = 8 \times 10^{-11}$ cm²/sec, which decreased to $D(x = 3 \times 10^{-2}) = 1 \times 10^{-11}$ cm²/sec with increasing H content of the layer.

IV. INTERPRETATION OF THE CONCENTRATION DEPENDENCE OF DIFFUSIVITY

Knowing the crystal structure of WO₃ to house channels of two different sizes,¹¹ one is inclined to bring this factor into any interpretation of the observed $D(x)$ curves. Two models will be tested here. First we investigate diffusion, which proceeds along independent parallel channels of different diffusion coefficients; then we turn to a percolation model.

$$D(y) = \frac{pD_1^{1/2} \exp(-y^2/4D_1) + (1-p)D_2^{1/2} \exp(-y^2/4D_2)}{pD_1^{-1/2} \exp(-y^2/4D_1) + (1-p)D_2^{-1/2} \exp(-y^2/4D_2)} \quad (7)$$

Inspection of Eq. (7) shows that an extremum function for $D(c)$ is predicted.

One might assume an independent two-channel diffusion with p depending on H content, c . The extremum shape

A. Diffusion along two independent channels

Let us investigate whether the observed $D(x)$ curves can be ascribed to diffusion which proceeds independently along two parallel channels with different but constant diffusion coefficients for each channel. The question is what kind of $D(c)$ curve is rendered by the Boltzmann method if diffusion is like this. Let D_1 and D_2 denote the diffusion coefficients, c_1 and c_2 the concentrations in the channels, and p and $(1-p)$ the proportions of channels 1 and 2, respectively. Then, considering Eq. (3), the two-channel diffusion can be written as

$$D(c)(dc/dy) = pD_1(dc_1/dy) + (1-p)D_2(dc_2/dy) \quad (6)$$

Since the relationship between concentrations $c = pc_1 + (1-p)c_2$ holds, one can express $D(y)$, bearing in mind Eq. (5), as

of $D(c)$ would be maintained just the same, except for the impossible $p(c)$ functions by which $p(c_0) \equiv 1$.

A numerical evaluation of Eq. (7) with $p = 0.5$ is given in Fig. 4. These curves being in apparent contradiction with

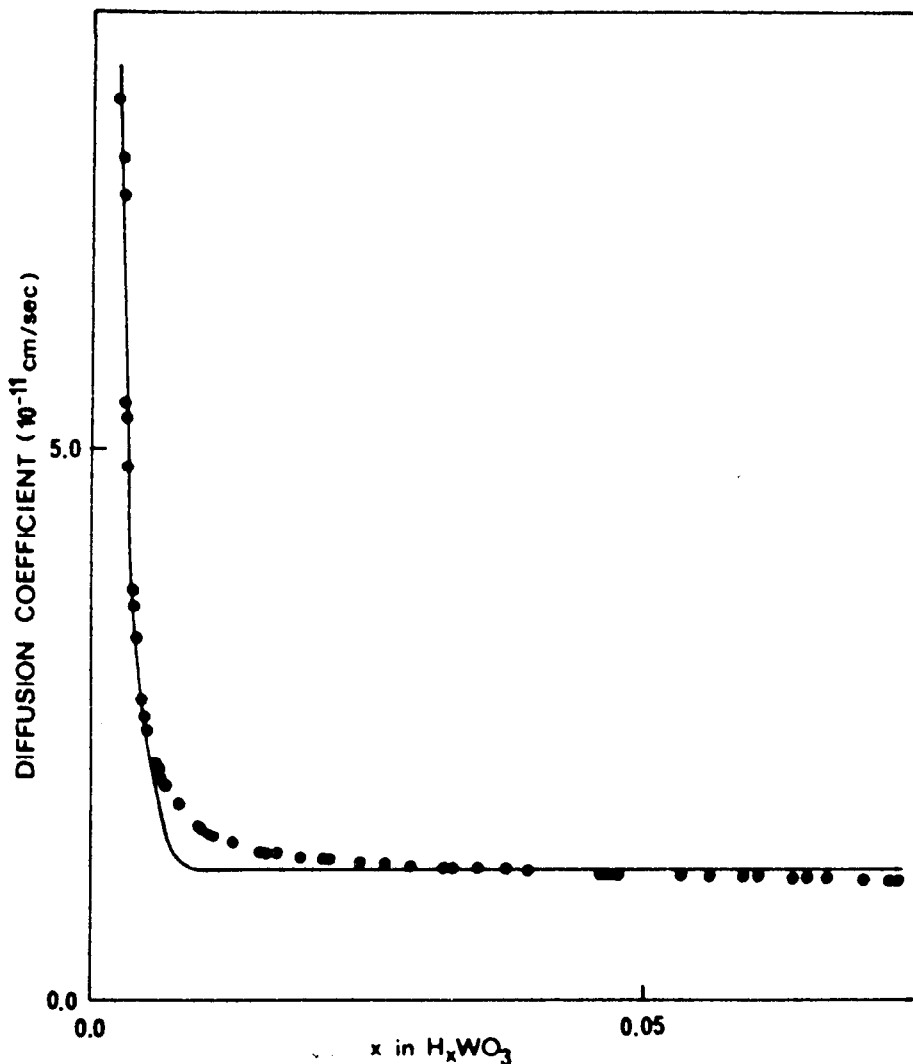


FIG. 3. Diffusion coefficient of H in H_xWO_3 layer vs H content. ●: measured. Solid curve: calculated by the modified percolation model, Eqs. (8)–(10). Fitted parameters: $D_m = 1.20 \times 10^{-11}$ cm²/sec; $D_0 = 2.7 \times 10^{-9}$ cm²/sec; $p_0 = 0.42$; $\alpha = 50.8$.

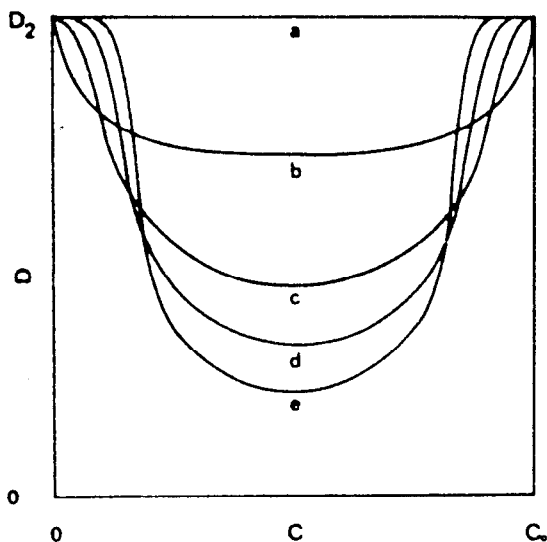


FIG. 4. Apparent concentration dependence of the diffusion coefficient for two independent channels with constant diffusivities, Eq. (7). (a) $D_2/D_1 = 1.0$; (b) $D_2/D_1 = 0.5$; (c) $D_2/D_1 = 0.2$; (d) $D_2/D_1 = 0.1$; (e) $D_2/D_1 = 0.05$; $p = 0.5$ for all cases.

our experimental findings (Fig. 3), one has to conclude that two-independent channel diffusion cannot account for our observations. It can be seen that the assumption of any number of independent channels would also fail to reproduce our findings.

B. Concentration-dependent percolation

The failure of independent channel diffusion in conjunction with the present problem prompted us to investigate two-channel diffusion with an allowance for the interaction of channels. The simplest way of describing diffusion along intertwining channels of different diffusivity is classical percolation,¹² which allows only for the geometrical properties of a two-component matrix without paying any heed to dynamic processes or to the nature of diffusing particles.

We propose the following model. Two kinds of channels are available for H in the lattice: one with high diffusivity D_0 , the other with a lower one, D_m . The volume fraction of the high diffusivity channel is denoted by p . The entrance of H atoms alters the WO_3 lattice in such a way that p decreases with increasing x . It is as if H atoms caused jamming in the fast channels, but much less so in the slow ones. For

the sake of simplicity, a linear relationship is assumed:

$$p(x) = p_0 - \alpha x, \quad (8)$$

where p_0 is the proportion of fast channels in pure WO_3 .

According to Landauer's¹³ effective medium percolation theory, the actual diffusion coefficient D is related to p as

$$D = D_0[b + (b^2 + r/2)^{1/2}], \quad (9)$$

where

$$b = 0.5[(1.5p - 0.5)(1 - r) + 0.5], \quad (10)$$

and $r = D_m/D_0$.

We compared Eqs. (8)–(10) with our experimental results in Fig. 3. The solid curve, coinciding reasonably well with the experimental points, was adjusted by fitting D_m , D_0 , p_0 , and α . The errors in the parameters of the $D(x)$ curve determined from one single run were 10%, 60%, 16%, and 34%, respectively. The deviation of experimental and calculated curves near the x value, where D becomes virtually constant, can be regarded as support for the percolation model, since effective medium theory is known to overestimate the decrease of D near the percolation threshold. As mentioned in Sec. III, the reproducibility of different runs was much poorer; hence, the averages of the parameters over five subsequent runs are beset with considerably higher error limits. The results are $D_m = (1.07 \pm 0.31) \times 10^{-11} \text{ cm}^2/\text{sec}$, $p_0 = 0.49 \pm 0.09$, $\alpha = 28 \pm 16$, and for D_0 only an order of magnitude estimate can be proposed, viz., $D_0 \approx 10^{-9} \text{ cm}^2/\text{sec}$.

The extrapolated diffusivity in a virgin WO_3 lattice D_0 is seen to be some two orders of magnitude higher than the high concentration limit D_m . It is of interest that D attains

D_m at a composition as dilute as $x = 0.03$, although H_2 , WO_3 with a hydrogen content of $x = 0.5$ can be prepared.¹⁴

One can only speculate regarding the physical nature of the fast and slow channels. They might be identical with the two types of channels in the WO_3 lattice, and jamming of the channels then consists of H atoms finding stable sites in the crystal. It is also possible, however, that it is a competition between bulk and grain boundary diffusion, and the absorption sites of the grain boundary channels become saturated.

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