An Interpretation of the Elovich Equation for the Rate of Chemisorption on the Basis of Surface Heterogeneity

By Yutaka KUBOKAWA

(Received September 9, 1959)

Taylor and Thon[1] showed that a number of chemisorption rate data are represented by the Elovich equation

$$dq/dt = ae^{-bq}$$

where q is the amount of gas adsorbed and a and b are constants. In order to explain this equation, they postulated the annihilation of adsorption sites in the course of adsorption. Being stimulated by this work, various workers[2] discussed the applicability of this equation for chemisorption processes and presented various models leading to this equation. Although there is, of course, no reason to believe that only one and the same mechanism is operative in all systems to which the Elovich equation is applicable, the most probable interpretation of the equation seems to be the one based on surface heterogeneity at least for the adsorbents for which the existence and the effect of surface heterogeneity have been established.

Such an interpretation has been proposed by Porter and Tompkins[2] for a simple case where the distribution function of adsorption site is constant and the rate of desorption is negligibly small. The purpose of the present paper is to elaborate a similar interpretation for more complex cases where the distribution is variable and/or the rate of desorption can not be neglected and to discuss some available data with respect to the variation of constant b in the Elovich equation with pressure and temperature.

Adsorption Rate on a Heterogeneous Surface.—For a heterogeneous surface the adsorption sites over the whole surface may be divided into a number of sets, each of which consists of sites of the same kind; the number of sites in each set is given by a distribution function which may, in the present case, be assumed to be a function of the activation energy E for a given chemisorption. Taking account of desorption, the net rate of adsorption on any set of sites may be given by

$$v = d\theta/dt = kp(1-\theta) - k'\theta$$

where θ is the fraction of the sites covered and p the pressure in the gas phase. Since $\theta = 0$ when $t = 0$, this rate gives on integration at a constant pressure

$$\theta = \theta_e[1 - e^{-(kp+k')t}]$$

where θ_e is the equilibrium coverage. Differentiating with respect to time

$$v = (kp+k')\theta_e e^{-(kp+k')t} = kpe^{-(kp/\theta_e)t} \qquad (1)$$

The rate for the whole surface may be obtained by integration, by assuming a continuous distribution function of sites. First, let us consider the simplest case where desorption is negligible and the distribution function N is constant. Since $\theta_e = 1$ in this case, Eq. 1 becomes

$$v = Ke^{-Kt} \qquad (2)$$

where $K = kp$. The rate for the whole surface under such conditions will be

$$N\int_0^\infty v(E)dE = N\int_\infty^0 [v(E)dE/dK]dK \qquad (3)$$

From the expression $k = \text{const.}\ e^{-E/RT}$, it follows that

$$dE/dK = -\boldsymbol{R}T/K \qquad (4)$$

Introduction of Eqs. 2 and 4 into Eq. 3 gives

$$N\int_0^\infty v(E)dE = -N\boldsymbol{R}T\int_\infty^0 e^{-Kt}dK = N\boldsymbol{R}T/t \quad (5)$$

On the sites with a high value of E the rate will naturally be small, while on those with a low value of E it will again be small because the coverage is here close to the equilibrium value. For a particular set of sites with an intermediate magnitude of E, therefore, the rate will pass through a maximum. This condition may be written as

$$\frac{dv}{dE} = \frac{dv}{dK}\frac{dK}{dE} = e^{-Kt}(1-Kt)\left(-\frac{K}{\boldsymbol{R}T}\right) = 0$$

Consequently, v shows a maximum at $Kt = 1$. The maximum rate, being equal to NKe^{-1} or N/te, is proportional to the rate over the whole surface represented by Eq. 5.

When the distribution function is not constant and the rate of desorption can not be ignored, the over-all rate can not easily be integrated. However, it may be assumed as a first approximation that in this case the over-all rate is also

---

[1] H. A. Taylor and N. Thon, *J. Am. Chem. Soc.*, **74**, 4169 (1952).

[2] A. S. Porter and F. C. Tompkins, *Proc. Roy. Soc.* **A217**, 529 (1953); H. J. Engell and K. Hauffe, *Z. Elektrochem.*, **57**, 762 (1953); R. T. Landsberg, *J. Chem. Phys.*, **23**, 1079 (1955); D. D. Eley, *Trans. Faraday Soc.*, **49**, 643 (1953) etc.

proportional to the maximum rate.

As described above, the rate for any set of sites can be represented by

$$v=NK\mathrm{e}^{-Kt/\theta}$$

where θ is written for θ_e for brevity. The condition for the maximum rate is

$$\frac{\mathrm{d}v}{\mathrm{d}E}=\frac{\mathrm{d}v}{\mathrm{d}K}\frac{\mathrm{d}K}{\mathrm{d}E}=\left(-\frac{K}{\boldsymbol{R}T}\right)N\mathrm{e}^{-Kt/\theta}\left[1+\frac{\mathrm{d}N}{N}\frac{K}{\mathrm{d}K}\right.$$

$$\left.-Kt\frac{\mathrm{d}(K/\theta)}{\mathrm{d}K}\right]=0$$

The dependence of K on θ is determined by the relation between the activation energy of adsorption E and the heat of adsorption Q, which is assumed to be given by

$$E-E_0=(1/\alpha)(Q-Q_0)$$

where α is a constant and Q_0 is the heat of adsorption on the sites with the lowest activation energy E_0. Assuming the Langmuir isotherm to be applicable,

$$1/\theta=1+(A/P)\mathrm{e}^{-Q/\boldsymbol{R}T}$$

so that

$$\frac{\mathrm{d}(1/\theta)}{\mathrm{d}(-Q/\boldsymbol{R}T)}=\frac{A}{p}\mathrm{e}^{-Q/\boldsymbol{R}T}=\frac{1}{\theta}-1$$

It follows then

$$\frac{\mathrm{d}\theta}{\mathrm{d}K}=\frac{\mathrm{d}\theta}{\mathrm{d}(1/\theta)}\frac{\mathrm{d}(1/\theta)}{\mathrm{d}(-Q/\boldsymbol{R}T)}\frac{\mathrm{d}(-Q/\boldsymbol{R}T)}{\mathrm{d}(-E/\boldsymbol{R}T)}\frac{\mathrm{d}(-E/\boldsymbol{R}T)}{\mathrm{d}K}$$

$$=\alpha\left(\frac{1}{\theta}-1\right)\left(-\frac{\theta^2}{K}\right) \qquad (6)$$

Hence

$$\frac{\mathrm{d}(K/\theta)}{\mathrm{d}K}=\frac{1}{\theta}-\frac{K}{\theta^2}\frac{\mathrm{d}\theta}{\mathrm{d}K}=\frac{1+\alpha-\alpha\theta}{\theta}$$

By defining $\beta=(\mathrm{d}N/N)(K/\mathrm{d}K)$, we find that the rate v shows a maximum at

$$Kt=[(1+\beta)\theta]/(1+\alpha-\alpha\theta)=F\theta \qquad (7)$$

where $F=(1+\beta)/(1+\alpha-\alpha\theta)$. So that the maximum rate v_m is

$$v_m=NK\mathrm{e}^{-F} \qquad (8)$$

Taking the logarithm of Eq. 8 and differentiating it with respect to $\ln K$

$$\frac{\mathrm{d}\ln v_m}{\mathrm{d}\ln K}=1+\beta-\frac{\mathrm{d}F}{\mathrm{d}\ln K}$$

Hence, we may write,

$$\frac{\mathrm{d}\ln v_m}{\mathrm{d}q}=\frac{\mathrm{d}\ln v_m}{\mathrm{d}\ln K}\frac{\mathrm{d}\ln K}{\mathrm{d}E}\frac{\mathrm{d}E}{\mathrm{d}q}$$

$$=\left(1+\beta-\frac{\mathrm{d}F}{\mathrm{d}\ln K}\right)\left(-\frac{1}{\boldsymbol{R}T}\right)\frac{\mathrm{d}E}{\mathrm{d}q} \qquad (9)$$

where q is the amount adsorbed at a given time. Taking the logarithm of Eq. 7, differentiating it with respect to time,

$$\frac{\mathrm{d}\ln K}{\mathrm{d}E}\frac{\mathrm{d}E}{\mathrm{d}t}+\frac{1}{t}=\frac{1}{F}\frac{\mathrm{d}F}{\mathrm{d}\ln K}\frac{\mathrm{d}\ln K}{\mathrm{d}E}\frac{\mathrm{d}E}{\mathrm{d}t}$$

$$+\frac{1}{\theta}\frac{\mathrm{d}\theta}{\mathrm{d}K}\frac{\mathrm{d}K}{\mathrm{d}E}\frac{\mathrm{d}E}{\mathrm{d}t} \qquad (10)$$

Inserting Eqs. 6 and 4 in Eq. 10, and rearranging

$$\frac{\mathrm{d}E}{\mathrm{d}t}=\left(\frac{\boldsymbol{R}T}{t}\right)\left(1+\alpha-\alpha\theta-\frac{1}{F}\frac{\mathrm{d}F}{\mathrm{d}\ln K}\right)^{-1} \qquad (11)$$

Using the definition of F, we can write Eq. 11 as

$$\frac{\mathrm{d}E}{\mathrm{d}t}=\left(\frac{\boldsymbol{R}T}{t}\right)F\left(1+\beta-\frac{\mathrm{d}F}{\mathrm{d}\ln K}\right)^{-1} \qquad (12)$$

Eqs. 7 and 8 give

$$v_m=(N/t)F\theta\mathrm{e}^{-F}$$

As was described above, a relationship $v_t=cv_m$ holds where v_t is the over-all rate and C a constant. Hence,

$$v_t=\frac{\mathrm{d}q}{\mathrm{d}t}=C(N/t)F\theta\mathrm{e}^{-F} \qquad (13)$$

comparing Eq. 12 with Eq. 13, we obtain

$$\frac{\mathrm{d}E}{\mathrm{d}q}=\frac{\boldsymbol{R}T}{CN\theta}\left[\frac{\mathrm{e}^F}{1+\beta-(\mathrm{d}F/\mathrm{d}\ln K)}\right]$$

Inserting this expression into Eq. (9)

$$\frac{\mathrm{d}\ln v_m}{\mathrm{d}q}=\frac{\mathrm{d}\ln v_t}{\mathrm{d}q}=-\frac{1}{CN\theta}\mathrm{e}^F \qquad (14)$$

When desorption is negligible and N is constant, Eq. 13 becomes

$$\mathrm{d}q/\mathrm{d}t=CN/t\mathrm{e}$$

Comparing this expression with Eq. 5, we obtain $C=\boldsymbol{R}T\mathrm{e}$. Hence, Eq. 14 becomes

$$\frac{\mathrm{d}\ln v}{\mathrm{d}q}=-\left(\frac{1}{N\theta\boldsymbol{R}T\mathrm{e}}\right)\mathrm{e}^F=-\left(\frac{1}{N\theta\boldsymbol{R}T\mathrm{e}}\right)\mathrm{e}^{\frac{1+\beta}{1+\alpha-\alpha\theta}} \qquad (15)$$

where v is written for v_t for the sake of simplicity of representation. Eq. 15 gives the physical meaning of constant b of the Elovich equation on the basis of surface heterogeneity.

Variation of the Constant *b* of the Elovich Equation with Temperature and Pressure.—For the sake of simplicity, let us assume the values of α and β to remain constant on changing pressure or temperature in the rate measurements, and discuss the dependence of b on temperature and pressure for the following four different cases.

Case 1: Desorption is negligible and N is constant. In this case Eq. 15 becomes

$$\frac{\mathrm{d}\ln v}{\mathrm{d}q}=-\frac{1}{N\boldsymbol{R}T}=\mathrm{const}$$

Accordingly, strict applicability of the Elovich equation is expected. As described by various workers[2)], the value of b should be independent of pressure and vary in proportion to $1/T$.

Case 2: Desorption is negligible but N is not constant. In this case Eq. 15 becomes

$$\frac{\mathrm{d}\ln v}{\mathrm{d}q} = -\left(\frac{1}{NRT}\right)e^{\beta}$$

The right hand side of this equation varies as adsorption proceeds. However, if the range of coverage is limited, and the change of N during adsorption is not marked, we may expect that the Elovich equation will still, though approximately, be obeyed. Variation in the value of b expected in this case may be as follows: If N increases with E, the value of N for the sites mainly responsible for adsorption may increase with pressure or temperature, since the set of sites with a higher value of E may be covered at a higher pressure or temperature. This increase of N will result in the decrease of b with increasing pressure or temperature.

Case 3: Desorption can not be neglected but N is constant. In this case, Eq. 15 becomes

$$\frac{\mathrm{d}\ln v}{\mathrm{d}q} = -\left(\frac{1}{N\theta R T\mathrm{e}}\right)e^{\frac{1}{1+\alpha-\alpha\theta}}$$

As described in Case 2, the Elovich equation will approximately be obeyed in a limited range of coverage. Let us consider the pressure dependence of b for the case $1<\alpha<2$, which seems to be the most probable case for α positive. Plotting $\theta e^{\frac{-1}{1+\alpha-\alpha\theta}}$ against θ for the two different values of α, $\alpha=1$ and $\alpha=2$, we obtain Fig. 1, which shows that, except in the range $\theta \simeq 1$, $\theta e^{\frac{-1}{1+\alpha-\alpha\theta}}$ increases with θ. This result together with the fact that the sites with a higher value of E, i.e., with a larger value of θ come to operate at a higher pressure leads to the conclusion that the value of b decreases with increasing pressure.

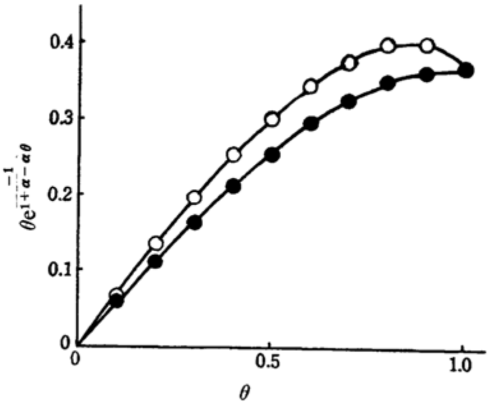

Fig. 1. Plot of $\theta e^{\frac{-1}{1+\alpha-\alpha\theta}}$ against θ.
—●—, $\alpha=1$; —○—, $\alpha=2$

Case 4: Desorption can not be neglected and, in addition, N is not constant. Let us consider only the special case when both conditions, $\mathrm{d}N/\mathrm{d}E>0$ and $1<\alpha<2$, are satisfied. Remembering that $\beta<0$ in this case, the following conclusion in the pressure dependence of b may be drawn. The extent of decrease of b with increasing pressure may be greater than that in the case where either N or θ alone varies, i.e., in Case 2 or 3 described above.

So far we have tacitly assumed an undissociative adsorption. For a dissociative adsorption, the adsorption rate corrected for desorption may be given by $k\sqrt{p}(1-\theta)-k'\theta$, or $kp(1-\theta)^2-k'\theta^2$. It is clear that the former equation leads to the same expression for the maximum rate as in the undissociative adsorption, except for the term $\sqrt{p}$. As regards the latter equation, it may also easily be shown that, in case desorption is negligible, this gives a similar expression for the maximum rate to that for the undissociative adsorption. It may therefore be expected that qualitative conclusions concerning the pressure dependence of b described in Cases 3 and 4 will not be altered for the dissociative adsorption.

A Criterion for the Negligible Desorption.—It follows from Eq. 15 that

$$\frac{-\mathrm{d}(\ln v-\ln v_0)}{\mathrm{d}q} = \frac{e^{\frac{1+\beta}{1+\alpha-\alpha\theta}}}{N\theta R T\mathrm{e}} = \frac{e^{\gamma}}{N\theta R T}$$

where $\gamma=(1+\beta)/(1+\alpha-\alpha\theta)-1$ and v_0 represents the initial rate when $t=0$ or $q=0$, that is, the adsorption rate on the set of sites with the lowest value of E. Integration of this equation gives

$$q = RT\int N\theta e^{-\gamma}\mathrm{d}(\ln v_0-\ln v)$$

Substituting the expression, $\ln v_0=\ln p+\ln v_0'$, where v_0' represents the pressure independent terms in v_0, we obtain

$$q = RT\int N\theta e^{-\gamma}\mathrm{d}\,[\ln v_0'-(\ln v-\ln p)]$$

This equation leads to the conclusion that if desorption can be neglected, i.e., the conditions $\theta=1$ and $\gamma=\beta$ are satisfied, the plots of q against $\ln v-\ln p$ at different pressures should lie on the same curve, provided that the temperature is constant. On the contrary, if desorption is not negligible, such plots will give separate curves.

Discussion of Some Available Data with Respect to Variation of b with Pressure.—*1) Hydrogen on Zinc Oxide.*—Values of constant b for this system were obtained from the following integrated form of the Elovich equation

$$q=(2.3/b)\log(t+t_0)-(2.3/b)\log t_0,\quad t_0=1/ab$$

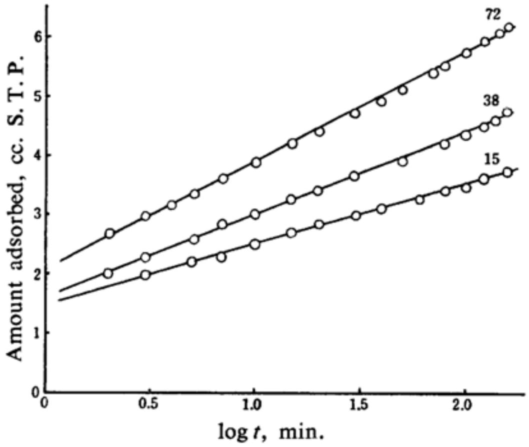

Fig. 2. Elovich plots for the hydrogen chemisorption on zinc oxide at 140°C. Figures indicate the initial pressure in mmHg.

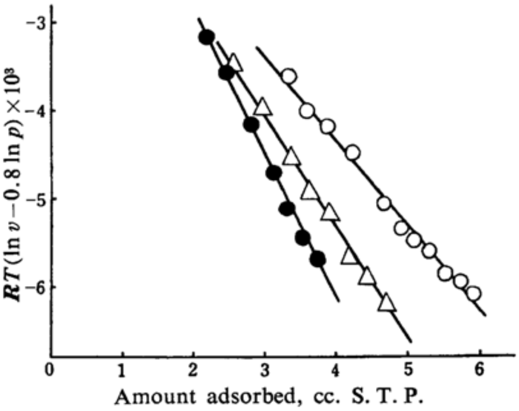

Fig. 3. Plots for the hydrogen chemisorption on zinc oxide at 140°C. —○—, 72 mmHg; —△—, 38 mmHg; —●—, 15 mmHg.

Plotting $\log(t+t_0)$ against q with t_0 adjusted to give a linear plot, the value of b was determined from the slope. The results shown in Fig. 2 indicate that the slope $2.3/b$ increases with initial pressure[3].

The same data are shown in Fig. 3 as the plots of q against $\ln v - 0.8 \ln p$. The term $\ln p$ is here multiplied by a factor of 0.8, for the rate was found to be proportional to $p^{0.8}$ as reported previously[4]. As seen in this figure, the plots at different pressures give distinctly separate curves, indicating that appreciable desorption takes place during adsorption rate measurements, which is also expected from the results described in the previous paper[4].

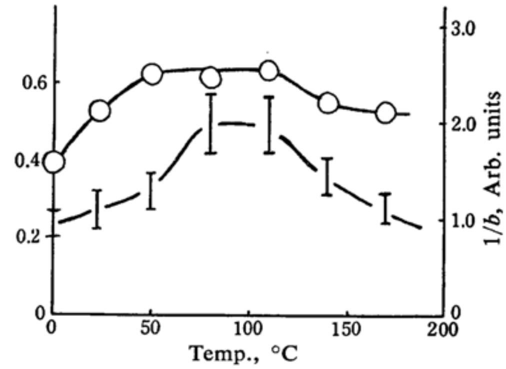

Fig. 4. Variation with temperature of the exponent n and $1/b$ at the pressure 65 mmHg. —I—, n; —○—, $1/b$

The pressure dependence of $1/b$ for this chemisorption was found to be approximately represented by $1/b \propto p^n$. As shown in Fig. 4, the exponent n varies with temperature and passes through a maximum, indicating that the pressure dependence of $1/b$ is considerably influenced by temperature. As given together in the figure, $1/b$ itself obtained at a particular pressure shows a similar dependence on temperature. It seems impossible to explain such behavior in terms of the concept that only the value of θ varies with pressure but the distribution function N is constant[5]. It may therefore be concluded that hydrogen chemisorption on zinc oxide belongs to the case where both N and θ change, i. e., to Case 4.

2) Hydrogen on Chromic Oxide Gel.—As an example for the case where the rate of desorption is negligibly small, we may mention the chemisorption of hydrogen on chromic oxide gel investigated by Burwell and Taylor[6]. Taking into account that the rate of adsorption for this system was found to be proportional to $p^{0.8}$ by these investigators, their data have been reexamined by plotting q against $\ln v - 0.8 \ln p$ with the results shown in Fig. 5. As seen in the figure, all of the plots at different pressures lie on a single curve. In addition, $-\mathrm{d} \ln v/\mathrm{d}q$ increases with decreasing value of E[7]. We

---

[3] The adsorption rate was measured by pressure change, using an adsorption apparatus of constant volume. The pressure decrease due to adsorption was no more than 10~20% of the initial pressure. The latter quantity was measured one minute later than the time of admission of hydrogen into the vessel.

[4] Y. Kubokawa, This Bulletin, 33, 550 (1960).

[5] If the value of θ alone were variable, such a marked increase in n with increasing temperature from 20 to 80°C as seen in Fig. 4 would be accompanied by decrease in $1/b$ at a particular pressure, in contradiction to what was observed.

[6] R. L. Burwell and H. S. Taylor, *J. Am. Chem. Soc.*, 58, 697 (1936).

[7] Strictly speaking, this conclusion is valid provided that β is unaltered with decreasing value of N. Even if β is altered, however, it seems unlikely that the decrease in e^{β} offsets the effect of the decrease in N, since in most cases $|\beta|$, i. e., $|\mathrm{d}\ln N/\mathrm{d}\ln K|$ may be less than 1, and the change of β may be small compared with that of N. It will be shown in a later paper that the inference given here is reasonable for this adsorption.

may therefore regard this chemisorption as an example for Case 2 with N increasing with E. In fact, the value of b obtained by applying the integrated form of the Elovich equation decreases with increasing pressure as shown in Table I, in accordance with the above statement.

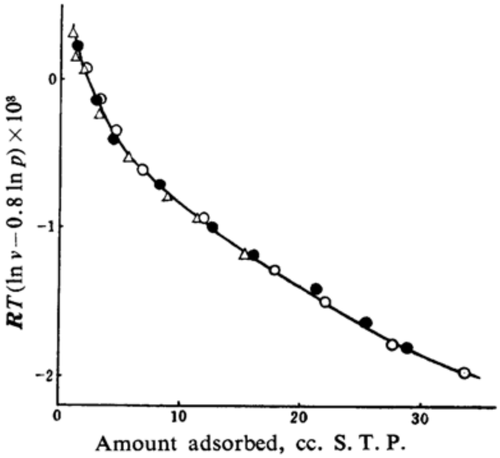

Fig. 5. Plots for the hydrogen chemisorption on chromic oxide gel at 457°K.
—○—, 1 atm.; —●—, 0.5 atm.; —△—, 0.25 atm.

TABLE I. VALUES OF b OBTAINED FROM THE INTEGRATED FORM OF THE ELOVICH EQUATION FOR THE HYDROGEN CHEMISORPTION ON CHROMIC OXIDE GEL AT 457°K

Pressure, atm.	b, 1/cc.
1	0.061
0.5	0.065
0.25	0.091

On the Constant t_0 in the Integrated Form of the Elovich Equation.—As described in a previous section, if desorption is negligible and N is constant, we may write

$$\mathrm{d}q/\mathrm{d}t=\boldsymbol{RTN}/t$$

Hence,

$$\mathrm{d}\ln t/\mathrm{d}q=(\mathrm{d}\ln t/\mathrm{d}t)(\mathrm{d}t/\mathrm{d}q)=1/\boldsymbol{RTN}$$

It is clear from this equation that, in this case, the plot $q-\log t$ is linear. Consequently, the constant t_0 in the integrated form of the Elovich equation should be very small in this case. Furthermore, as described above, Case 1 is the only case to which the Elovich equation is expected to apply strictly. We may therefore conclude as follows: So far as the present interpretation of the Elovich equation is applicable, the constant t_0 of an appreciable magnitude such as is frequently employed to make the plot $q-\log(t+t_0)$ linear implies that in such cases, the equation holds only approximately, and the constant b thus determined can not be given any physical meaning such as stated above, although the equation may be useful for evaluating initial rates.

Summary

For the heterogeneous surface where the distribution function was variable and/or desorption could not be neglected, the rate of adsorption was derived and the physical meaning of constant b in the Elovich equation was given. It was shown that in complicated case the Elovich equation is expected to apply only approximately in a limited range of coverage. The variation in constant b with pressure or temperature was qualitatively explained in terms of the concept that on changing pressure or temperature, different sets of sites are covered and/or the contribution of desorption in adsorption rate measurements, is altered. The chemisorption of hydrogen on zinc oxide and on chromic oxide gel was discussed on the basis of the present interpretation of the Elovich equation. Finally, it was shown that, on the basis of surface heterogeneity, the constant b obtained from the integrated form of the Elovich equation can not be given any physical meaning when the constant t_0 of an appreciable magnitude is required.

The author wishes to express his sincere thanks to Professor O. Toyama for his guidance and encouragement throughout the course of this study.

Department of Applied Chemistry
College of Engineering
University of Osaka Prefecture
Sakai-shi, Osaka