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The Kinetics of Adsorption of Carbon Monoxide, Hydrogen, and Oxygen on Finely Divided Nickel Oxide

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The adsorption of CO, H_2, and O_2 on NiO at 25°C has been studied with a constant-volume system and is found, in all cases, to obey the Elovich equation, with constants α and β which are strongly dependent on the initial pressure. In the case of H_2 and CO adsorption, α is also sensitive to the presence of excess oxygen irreversibly held at 200°C. CO adsorption isotherms, however, show no dependence on excess oxygen content. The initial rate of adsorption of hydrogen is found to be proportional to the square root of the pressure, indicating dissociative adsorption with a rate-limiting process involving the hydrogen atom. A brief, critical, review of theoretical interpretations of Elovich kinetics is given. None of these can account for the hydrogen and oxygen adsorption kinetics. The adsorption of CO on stoichiometric (yellow-green) NiO is in satisfactory agreement with the kinetic equation of Sutherland and Winfield for a rate-limiting Knudsen diffusion mechanism.

1. INTRODUCTION

As shown in a thorough review by Low (*1*), the rate of adsorption of gases on solids is often found to obey the Elovich equation,

$$dq/dt = \alpha \exp(-\beta q) \qquad (1)$$

where α and β usually depend on temperature and pressure. With regard to nickel oxide, such kinetics have been reported for the adsorption of oxygen (*2–7*), carbon monoxide (*7–10*) and hydrogen (*5, 11, 12*), although other kinetics have also been proposed (*3, 7, 13*).

The present communication is concerned with the room-temperature adsorption of CO, H_2, and O_2 on finely divided NiO. The same oxide sample was used throughout the measurements, so that the behavior of the three gases might be more readily compared. These measurements were part of an investigation concerned chiefly with the effects of pre-exposure to Co^{60} γ rays on the catalytic and adsorptive properties of NiO (*14, 15*).

2. THEORETICAL INTERPRETATIONS OF ELOVICH KINETICS

Although no attempt is made to mention every worker who has made useful contributions to the subject, it is intended to mention all distinguishable theoretical models, apart from that of Meller (*16*), which appears to be of too limited application (see ref. *1*).

With the foregoing exception, every model assumes the validity of the conventional kinetic formulation of the rate of reaction between a gas and a set of unoccupied adsorption sites. In all cases, furthermore, the rate of desorption is taken to be negligible, so that

$$dq/dt = kPn \qquad (2)$$

where kP is proportional to the rate of collision of gas molecules with the surface and n is the instantaneous number of unoccupied sites. Further developments may be divided into two classes, depending on whether n or k is taken to be an exponential function of q.

Models of the first class simply assume (*17–19*) that the expression

$$n = n_0 \exp(-\beta q) \qquad (3)$$

is satisfied rather than the usual conservative relation $n = n_0 - q$ (n_0 is constant). Equation (1) is obtained directly from (3) and (2). Various mechanisms have been proposed to account for (3) (*17–19*).

Models of the second class (*20–24*) permit Eq. (1) to be derived from Eq. (2) by allowing the activation energy of adsorption to increase linearly with coverage, so that k rather than n is an exponential function of q. It is necessary however, to restrict q to values much smaller than n_0 in order that n remain approximately constant. Several mechanisms have been proposed to account for a linear dependence of activation energy on coverage and two of these have received considerable attention. The more satisfying of the two, theoretically, is based on independently established solid state theory and applies to adsorption on semiconducting materials, where the boundary layer theory is used to provide a mechanism for "induced heterogeneity" (*25*). A kinetic expression similar to (*1*), however, is obtained only for cumulative (acceptor molecule on *p*-type surface or donor on *n*-type) and not for depletive chemisorption (*21*), except when the "induced" change in the activation energy is considerably less than kT (*26*). Even in the cumulative case, moreover, the similarity is rather forced, since the pre-exponential factor obtained is proportional to $1/q^2$ and it is necessary to neglect this substantial dependence on q in order to obtain the Elovich expression, Eq. (1). It may be noted, in addition, that considerable uncertainty exists (*5*, *6*) regarding the applicability of the boundary layer model to NiO, which fails to conform to the band theory of conduction (*27*).

The second well-known model leading to a linear dependence of activation energy on coverage requires the surface to be *a priori* heterogeneous with respect to the activation energy of adsorption. This model has recently been discussed in detail (*29*).

With regard to the present work, it must be emphasized that every interpretation mentioned above is restricted to adsorption at constant pressure and cannot strictly account for Elovich kinetics observed under constant-volume conditions, with pressures falling to as little as 10% or 20% of their initial values. Neither can any of them account for the frequently observed tendency (*1*, *2*, *19*, *30*) for β to decrease with increasing initial pressure. The last remark applies with equal force to the interpretation of Cimino *et al.* (*19*), regardless of claims to the contrary (*19*, *31*), as close inspection of Eq. (3) of ref. (*19*) will show.

An interpretation which is free from the above limitations remains to be considered and will be referred to as the Knudsen flow mechanism. The model is quite distinct from those already mentioned, since gaseous diffusion rather than the act of adsorption is the rate-limiting process. For the special case of transient Knudsen diffusion into "pores" (interparticle channels) accompanied by relatively fast establishment of adsorption equilibrium on the pore walls, Sutherland and Winfield (*32*) have derived the approximate expression,

$$P/P_0 = \exp(at)[1 - \operatorname{erf}(at)^{1/2}] \qquad (4)$$

which is expected to be valid over little more than the first half-life of the adsorption. P_0 is the initial pressure and the constant, a, contains all of the relevant physicochemical characteristics of the system. The Knudsen flow mechanism is of particular interest here, since it leads to Elovich-like kinetics under constant-volume conditions and alone predicts an inverse relation between β and the initial pressure. The model is furthermore unique in permitting a purely theoretical evaluation of β. The notation used in (4) is that of Freund (*33*), who first pointed out that adsorption data which satisfy (4) can be shown to be in reasonable agreement with the integrated form of Eq. (1). For present purposes, a suitable integrated form is obtained by substituting $V(P_0 - P)/RTA$ for q, whereupon (1) leads to,

$$\frac{P}{P_0} = \left[1 + \left(\frac{RTA}{\beta P_0 V}\right)\ln t_0\right] - \left(\frac{ART}{\beta P_0 V}\right)\ln(t + t_0) \qquad (5)$$

where $t_0 = 1/\alpha\beta$. When Elovich kinetics are obeyed, (5) shows that a plot of P/P_0 against $\log(t + t_0)$ can be made linear by a suitable choice of t_0. As noted by Freund (*33*), such is also the case when the kinetic data satisfy (4). The writer has found, however, that data generated by (4) can be linearized only for $P/P_0 < 0.8$. At smaller times (larger P/P_0), the Elovich process appears to be preceded by a much more rapid one, so that extrapolation to zero time gives nonzero values of q (see Fig. 3). Such behavior is frequently observed* (*17*, *19*). The form of (4) is such that the Elovich slope, $d(P/P_0)/d \ln (t + t_0)$, is independent of the value of a and is therefore the same for all systems. The constant β may thus be estimated from a plot of P/P_0 against $\log (t + t_0)$, using pressure–time data generated by (4) with any arbitrary a. The fixed slope is seen from (5) to be $2.3\, RTA/\beta VP_0$, so that β will be found to be inversely proportional to P_0 when the Knudsen flow model is applicable.

3. EXPERIMENTAL

NiO. Finely divided nickel oxide was prepared by the method of Teichner *et al.* (*34*), described in detail elsewhere (*14*). The product was yellow-green and turned immediately black on exposure to air at room temperature. The black oxide was stored over $CaCl_2$ for 20 months before use. After prolonged outgassing at 200°C, the BET surface area (N_2 at -196°C) became constant at 135 m^2g^{-1}.

Gas preparation. Oxygen was obtained by thermal decomposition of carefully outgassed crystals of $KMnO_4$ and passed through two traps at -196°C.

Carbon monoxide of high purity was obtained from a commercial supplier (L'Air Liquide) and was passed through two traps at -196°C before use.

Hydrogen was purified by diffusion through a heated palladium thimble, followed by a trap at -196°C.

Apparatus. The apparatus was of a conventional type, constructed entirely of Pyrex glass. The amount adsorbed was obtained from the change of pressure in a closed volume equivalent to 553 ml at 25°C when corrected for the temperature of the traps. In addition to the small sample bulb and two cold traps, the closed volume contained a multiple-range McLeod gauge (10^{-5} to 3 mm Hg). The 1.0 g sample was isolated from tap grease by means of a trap at -196°C and from mercury vapor by two such traps in series. A two-stage diffusion pump followed by a calibrated volume (3.5 liters) enabled desorption measurements to be made.

Experimental procedure. A single sample (1.0 g) was employed for all of the measurements to be described and was thus in permanent communication with a trap at -196°C over a period of 5 months. All adsorption measurements were made at 25°C. Before adsorbing the first dose of a given gas, the sample was pumped down at 200°C for 16 hr. Subsequent doses were added (in the order of increasing pressures, unless otherwise stated) when the pressure had fallen to less than 10^{-5} mm Hg or to a steady value. The latter applies particularly to the adsorption of CO, for which four isotherms were successively determined, each preceded by the normal outgassing procedure at 200°C.

Carbon monoxide was the first gas to be adsorbed on the black oxide, aged 20 months in dry air before outgassing. After the third CO isotherm, the color of the oxide had changed to yellow-green, indicating reduction to a near-stoichiometric composition. When the CO adsorption measurements were terminated, oxygen adsorption was studied, followed by hydrogen adsorption on the black oxide carrying a known amount of bound oxygen. In all cases, the first pressure reading was made 1 min after admission of the gas to the sample, so that values of t_0 less than about 0.3 min could not be estimated with accuracy.

Calculations. When Eq. (1) gives the rate of adsorption in moles per minute per square meter of surface, the units of α and β are mole min^{-1} m^{-2} and $mole^{-1}$ m^2, respectively. The value of β is obtained from the slope $(-2.3\, ART/\beta VP_0)$ of the Elovich

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* With regard to the rapid initial adsorption which may precede the establishment of Elovich kinetics, a certain confusion is apparent in the literature. It may be noted that $t_0 = 0$ is equivalent to an infinite (impossible) initial rate of adsorption (*29*) so that t_0 must be finite, although it may be immeasurably small. Only when t_0 is measurable, furthermore, can the $\log (t + t_0)$ plot be extrapolated to $t = 0$ and only in such cases can it be ascertained whether or not Elovich kinetics are obeyed from zero time. When t_0 is not experimentally accessible, no conclusion can be reached regarding the nature of the kinetic process at inaccessible times, in contradiction with some opinion (*24*) and practice (*5*).

plot and the pre-exponential factor, α, from the relation $t_0 = 1/\alpha\beta$.

4. RESULTS

A. Carbon Monoxide

Four consecutive series of adsorption measurements were made with CO, each series being preceded by the standard outgassing procedure at 200°C. In addition to rate measurements, four isotherms were obtained and are shown in Fig. 1, numbered in chronological order. The aged oxide contained 5.0 atom % of excess oxygen, of which about 50% to 60% [iodine method (*35*)] was not desorbed by the first outgassing, but was progressively removed, presumably as CO_2, by outgassing at 200°C after adsorption of CO. The sample had become yellow-green at the end of the third series of adsorption measurements. Although the isotherms appear insensitive to the concentration of excess oxygen, the latter had a very marked effect on the kinetics of adsorption. The longest time required for equilibrium to be reached in the first series was less than 2 hr, whereas more than 2 weeks was required for the last measurement of the fourth series. Most of the adsorption corresponding to the first two isotherms was too rapid to be followed. When adsorption was not too rapid, Elovich kinetics was observed. Values of β are shown in Fig. 2 as a function of the initial pressure. The corresponding series (isotherm) is indicated. In all cases, the initial rate of adsorption could not be calculated, since the linear plot did not extrapolate to $P = P_0$ at $t = 0$, but behaved as if the slow, Elovich adsorption was superimposed on a more rapid process which reached completion in a time of the order of t_0. Two examples of Elovich plots for CO, together with a "linearized" plot of data generated by Eq. (4), are shown in Fig. 3.

In accordance with classical kinetic theory, α may be expected, in the absence of dissociation, to be directly proportional to P, so that α/P_0, the "specific" pre-exponential factor, should be constant for a given state of the adsorbent surface. The limited data shown in Fig. 4 thus suggest that the rate of CO adsorption, at a given excess-oxygen content, is decreased by preadsorbed CO, a given quantity of the latter being more effective, the smaller the content of excess oxygen.

B. Oxygen

The adsorption of oxygen on the yellow-green oxide was too rapid to be followed with the present apparatus. When the residual pressure became measurable, however, the oxide had become gray-green and adsorption was relatively slow. An isotherm of limited range was obtained and is shown in Fig. 1. (The time required for a steady pressure to be reached exceeded 2 weeks at the highest pressure shown.) Elovich plots resembling those of Fig. 3 were found for the last two measurements (Fig. 1), but the vertical part of the curve near $t = 0$ was much longer (from 0.3 to 0.5 P/P_0). The Elovich constants obtained are given in Table 1, where values recalculated from the results of other workers are also included for later discussion. To facilitate comparison, α/P_0, rather than α, is given. The quantity of oxygen necessary to completely blacken the sample was estimated to be about 3 atoms per 100 surface nickel ions, which is about 10 times the figure given by Kuchynka and Klier (*4*).

The values of β recorded in Table 1 are shown in Fig. 5 as a function of P_0.

C. Hydrogen

Before adsorbing hydrogen, the excess oxygen content of the NiO was further increased to 1.86 cm^3 (STP) (assuming the yellow-green compound to be stoichiometric) by raising the temperature of the sample to 200°C in presence of oxygen. No further adsorption could be detected on cooling to 25°C and negligible desorption took place during subsequent outgassing at 200°C for 16 hr. Excellent Elovich plots were obtained for hydrogen adsorption at 25°C and the variation of β with P_0 is shown in Fig. 6. Two of the points at the low-pressure end of the curve were obtained from the last two rate measurements but one (see Fig. 8), showing that β is independent of the amount of hydrogen preadsorbed. Only the last rate measurement gave a measurable final pressure. A further dose of hydrogen

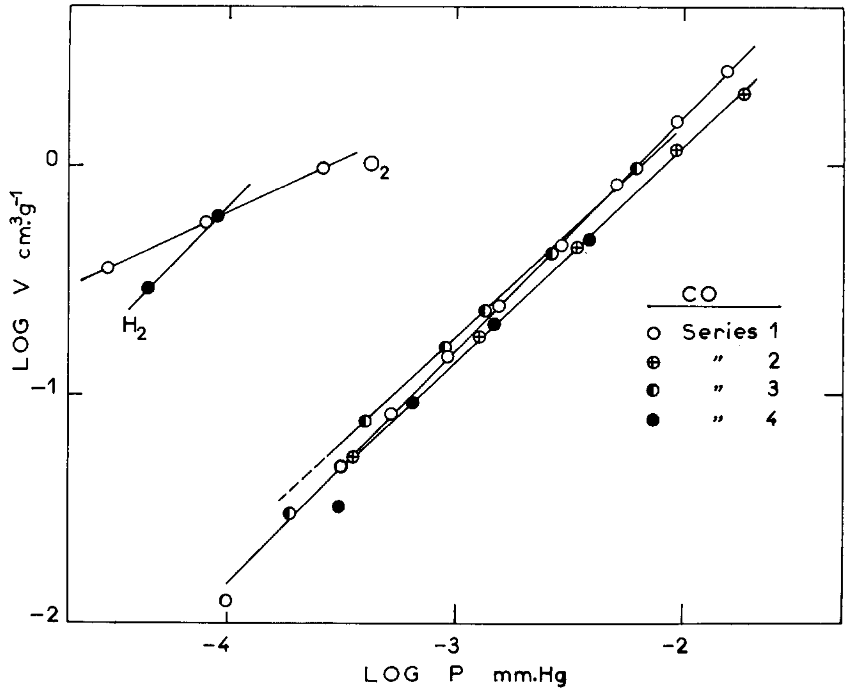

Fig. 1. Adsorption isotherms for CO, O_2, and H_2 on NiO at 25°C.

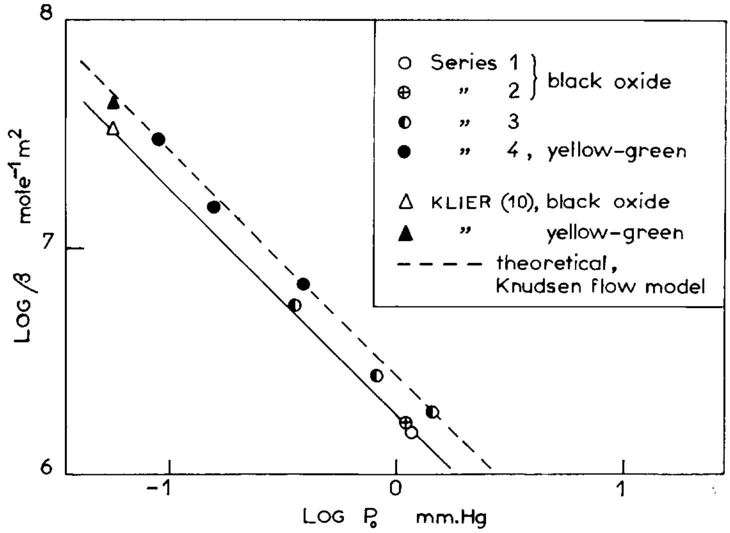

Fig. 2. Dependence of Elovich constant, β, on the initial pressure of CO.

was therefore added and allowed to equilibrate during 48 hr so that at least two points on the isotherm would be known. The result is shown in Fig. 1, together with the O_2 and CO isotherms. Measurable values of t_0 (0.4 to 10 min) were always obtained and Elovich kinetics were found to apply down to zero time, as shown by the examples given in Fig. 7. The pre-exponential factor, α, is thus the initial rate of adsorption and is

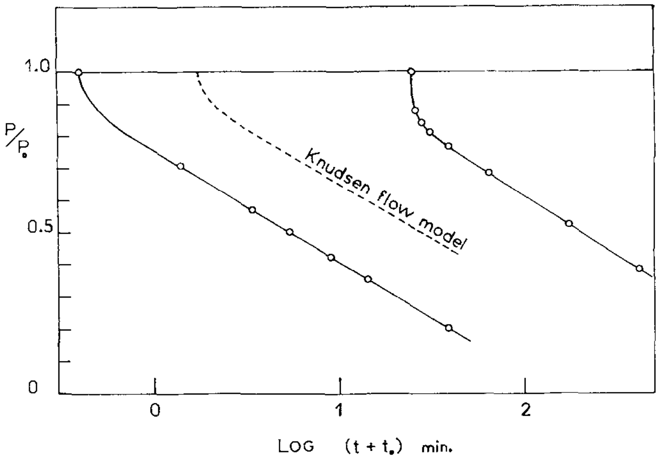

FIG. 3. Typical Elovich plots for CO adsorption. The dotted line represents a "linearized" plot of data generated by Eq. (4). Its position with respect to the horizontal axis depends on the value of a employed in (4).

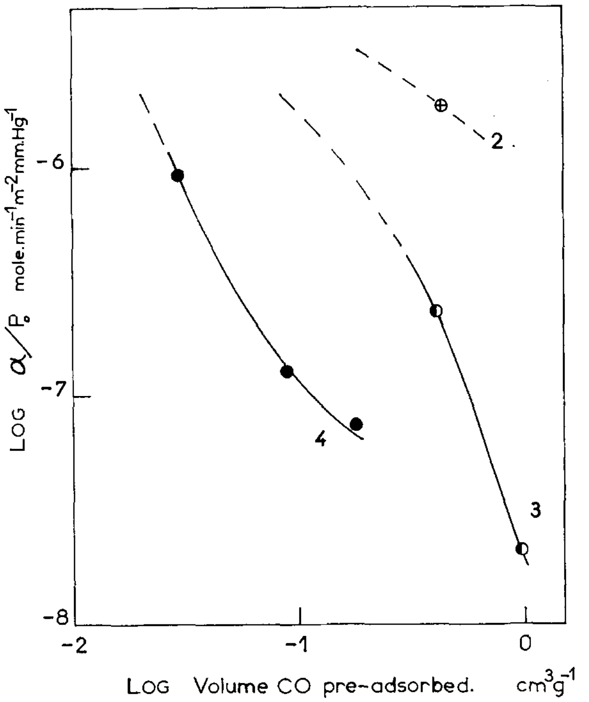

FIG. 4. Dependence of specific Elovich constant, α/P_0, on the amount of CO preadsorbed in Series 2, 3, and 4.

shown in Fig. 8 as a function of the initial pressure. The points are numbered in the order in which the measurements were carried out. Since the initial rates appeared to depend on the quantity of hydrogen preadsorbed, measurements 6 and 7 were made at relatively small values of P_0, in order that the hydrogen coverage should vary relatively little between successive measurements. The last three points thus show the variation of

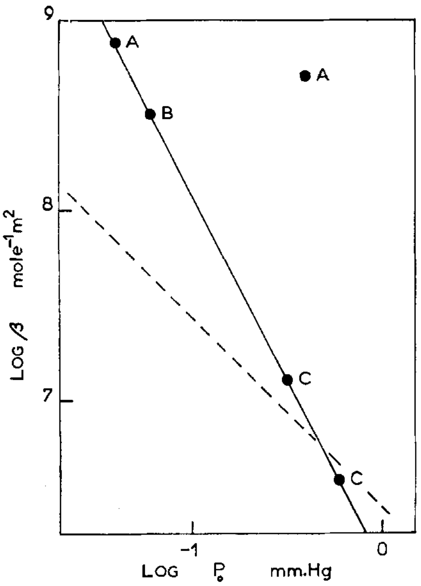

FIG. 5. Dependence of Elovich constant, β, on the initial pressure of O_2: A, results of Charman *et al.* (*5*); B, result of Haber and Stone (*6*); C, present work; - - -, Knudsen flow model.

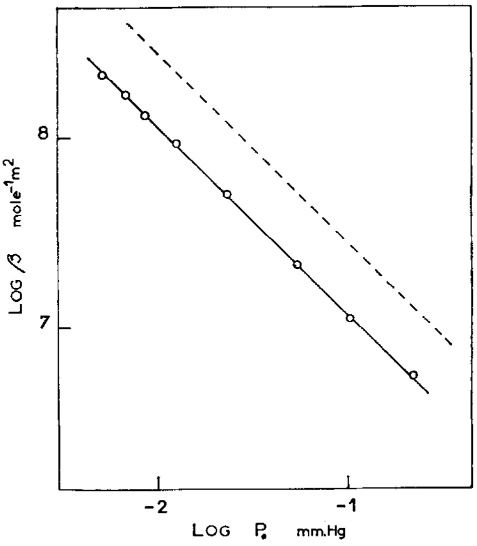

FIG. 6. Dependence of Elovich constant, β, on initial pressure of H_2: - - -, Knudsen flow model.

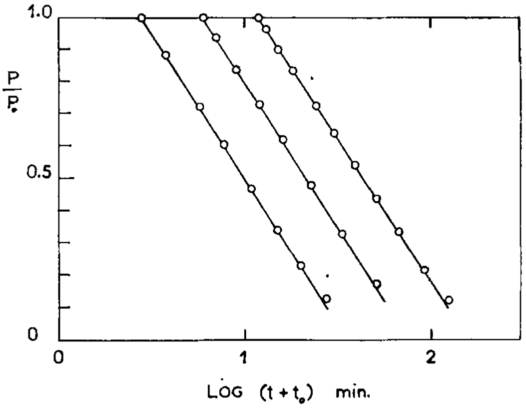

FIG. 7. Typical Elovich plots for hydrogen adsorption.

α with P_0 at approximately constant coverage of preadsorbed hydrogen and lie on a straight line of slope 0.49, from which it may be concluded that α is proportional to $P^{1/2}$. The effect of preadsorbed hydrogen on the initial rate may therefore be estimated from Fig. 9, where $\alpha/P_0^{1/2}$ is shown as a function of the amount of hydrogen preadsorbed. It appears from Fig. 9 that the effect of preadsorbed hydrogen on α had reached its maximum value when the last three measurements were made.

5. DISCUSSION

A. Carbon Monoxide

There is little doubt that the fourth series of CO adsorption measurements was carried out with an oxide of nearly stoichiometric composition. The total amount of CO which had been desorbed from the sample prior to the fourth series of measurements was 7.7 cm³, whereas the excess oxygen content of the original, outgassed sample was estimated to be about 4 cm³. These figures suggest that all of the CO adsorbed in the first three series was desorbed as CO_2, resulting in a progressive reduction of the sample. Complete reduction is also suggested by the agreement with the results of Klier (*10*) shown in Fig. 2. [The yellow-green oxide of Klier was prepared *in situ* from the hydroxide under severely controlled conditions (*4*)]. The effect of preadsorbed oxygen (150°) found by Klier was similar to that obtained in the present work and suggests that β for the black oxide should lie on the full line shown in Fig. 2.

Although simple thermodynamic arguments cannot be strictly applied in the case

TABLE 1
ELOVICH CONSTANTS FOR OXYGEN ADSORPTION ON NiO

Authors (ref.)	P_0 (mm Hg) T (°C) A (m^2g^{-1})	β ($mole^{-1}$ m^2)	α/P_0 [mole min^{-1} m^{-2} (mm $Hg)^{-1}$]	Remarks
Present work	0.32 25 135	1.25×10^7	6.2×10^{-8}	0.35 cm^3 (STP) of O_2 preadsorbed at 25°C
	0.59 25 135	3.65×10^6	1.9×10^{-9}	0.56 cm^3 (STP) of O_2 preadsorbed at 25°C
Charman, Dell, and Teale (*5*)	0.04 22 15.6[a]	7.6×10^8[a]	$\gtrsim 2.5 \times 10^{-7}$[a,b]	"Olive-green" oxide, outgassed at 550°C
	0.40 22 15.6[a]	5.0×10^8[a]	$\gtrsim 2.5 \times 10^{-8}$[a,b]	As above
Haber and Stone (*6*)	0.06 20 10.2	3.04×10^8[c]	1.2×10^{-7}[c]	Oxide presumably "green," outgassed at 450°C

[a] Average value for two preparations of NiO.

[b] From inspection of Fig. 1 of ref. (*5*), $t_0 \lesssim 0.1$ min.

[c] Values of Haber and Stone assumed to refer to 1.0 g sample.

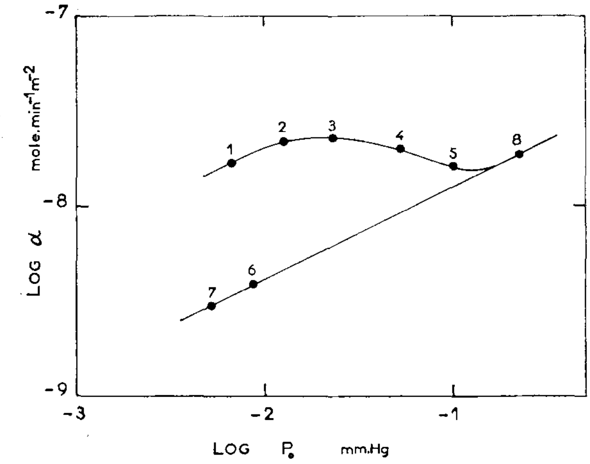

FIG. 8. Dependence of initial rate, α, on initial pressure of hydrogen. The numbers give the chronological order in which the measurements were made.

of partly irreversible process, the similarity of the four CO isotherms of Fig. 1 suggests, contrary to expectation (*10*), that the adsorption capacity and heat of adsorption are not appreciably altered by the progressive reduction of the sample. Unfortunately, the literature appears to contain no other room temperature isotherms of CO (or O_2) on NiO with which those of Fig. 1 might be compared. Recent calorimetric measurements (*36*) on a similar preparation of NiO, however, have shown that the heat of oxygen adsorption on the stoichiometric oxide is about twice that of CO adsorption. The rela-

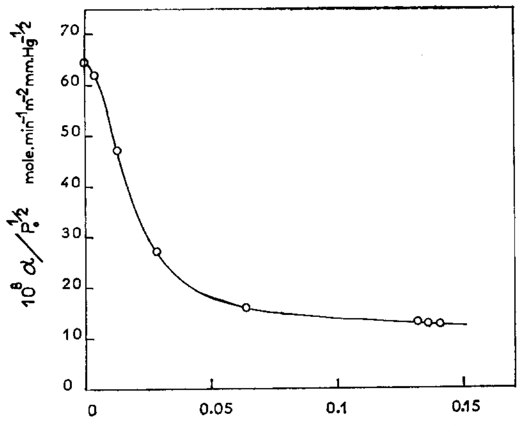

FIG. 9. Dependence of specific initial rate, $\alpha/P_0^{1/2}$, on the amount of hydrogen preadsorbed.

tive slopes of the O_2 and CO isotherms of Fig. 1 would indicate (*37*) that the same factor of 2 applies to the experiments reported here, so that the stoichiometric oxide produced by CO reduction of the black sample cannot be considered to behave exceptionally with regard to the energy of CO adsorption. Kubokawa and Toyama (*38*), in addition, found that the rate of CO desorption (NiO sintered at 700°C) was almost unaffected by pretreatment of the sample in oxygen at 450°C. In marked contrast, therefore, with oxygen freshly adsorbed at room temperature (*7, 36*), that which resists outgassing at 200°C is relatively inert with respect to CO. The latter, however, must interact in some way with the "excess oxygen,"* since the kinetics of adsorption are affected. As an alternative to the formation of different types of bonds (or adsorption complexes) with the same energy, it may be supposed that the excess oxygen simply catalyzes the adsorption process, altering the reaction path but not the final product. The results of Fig. 4, however, would indicate that the "catalyst" is progressively deactivated as CO is adsorbed. It might be supposed, for example, that the adsorption of CO on a surface Ni^{3+} ion, followed by immediate conversion of the latter to Ni^{2+} by electron capture from a neighboring cation (hole diffusion) is more rapid than direct adsorption on Ni^{2+}. The presence of the adsorbed CO in the neighborhood of the Ni^{3+} might then make the latter unavailable for further CO adsorption. Speculation along these lines would be more fruitful if comparative calorimetric as well as kinetic data were available for the appropriate stoichiometric and nonstoichiometric oxides.

The nature of the mechanism leading to Elovich kinetics will be considered later.

B. Oxygen

With the present results and those from two recent publications (*5, 6*), a quantitative comparison of kinetic data obtained by different workers can be undertaken (Table 1). Such comparisons are notoriously unsatisfactory where surface phenomena are concerned and the correlation suggested by the straight line of Fig. 5 was quite unexpected, considering the variety of experimental conditions involved. Since β is calculated from the rate of adsorption per unit area, the correlation suggests immediately that interparticle diffusion effects do not greatly influence the rate process when Elovich kinetics are established. If the excellent straight line of Fig. 5 is not fortuitous, β would appear to be insensitive to the state of the oxide surface but to have a pressure dependence close to $1/P_0^2$. In view of the higher pressure result (Fig. 5) of Charman *et al.*, however, additional measurements are needed to settle these questions. The values of α given in Table 1 are recorded only for possible future reference.

C. Hydrogen

The curve of Fig. 9 indicates that the effect of excess oxygen on the initial rate of adsorption is eliminated when the ratio of preadsorbed hydrogen to total excess oxygen is no more than about one hydrogen molecule per hundred oxygen atoms. Such a result suggests that all of the (presumably superficial) excess oxygen is not present in the same form. It would be of interest in this connection to measure chemically (*5, 35*) the Ni^{3+} content of samples carrying known

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* The term is loosely employed to designate any consequence of the presence of an excess of oxygen, for example, the presence of Ni^{3+} or of cation vacancies.

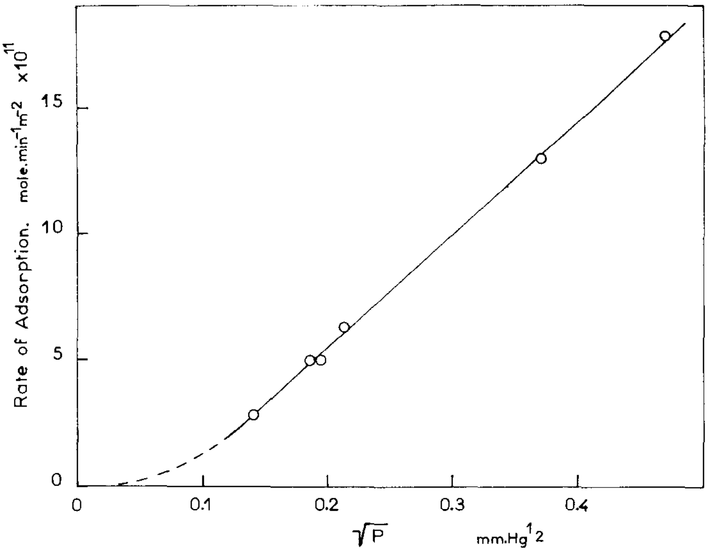

FIG. 10. Pressure dependence of rate of hydrogen adsorption on NiO at 40°C. Data of Cotton and Fensham (*7*).

amounts of oxygen irreversibly adsorbed at various temperatures. It is usually assumed that oxygen irreversibly adsorbed at higher temperatures is entirely ionic (*4*, *5*, *39*), but recent work (*40*, *41*) appears to cast considerable doubt on that assumption.

The calculation of the "specific" initial rates of Fig. 9 depends on the observation that the rate is proportional to the square root of the pressure. Since the linear part of Fig. 8 is based on the evidence of only three measurements, additional data have been sought in the literature. Suitable results have been found only in a recent article by Cotton and Fensham (*7*), where rates of adsorption at 40°C and pressures from 0.02 to 0.22 mm Hg are given (Table 2 of ref. *7*). The data in question* have been used to construct Fig. 10, where it may be observed that the rate appears to depend on P at lower pressures, but on $P^{1/2}$ over the greater part of the pressure range examined. Such a result, incidentally, is rather unexpected, since it implies a rate-limiting process involving atomic hydrogen, the latter being in near-equilibrium with the gas phase.

The Elovich constants obtained for hydrogen adsorption are in reasonable agreement with those calculated from the results of Charman *et al.* (*5*) and differ in a not unexpected direction from those which may be obtained from the results of Cotton and Fensham (*7*). The relevant data are shown in Table 2. The values in parentheses are from the present work and are taken from the curves of Figs. 6 and 8 at the appropriate pressures.

The data of Table 2 indicate that adsorption was relatively slow on the oxide prepared by Cotton and Fensham. Although that oxide gave reproducible results with regard to hydrogen adsorption, there is reason to suspect that its surface was relatively contaminated. Apart from the low outgassing temperature, it may be noted that the sample was not protected from a waxed, ground joint and was separated from the remainder of the apparatus by a trap at −76°C rather than at the lower temperature (−196°C) employed by Charman *et al.* and the writer.

Cotton and Fensham concluded that Elovich kinetics were not obeyed for hydrogen absorption, since it was observed that the rate fell rapidly to a constant value or was constant from zero time (the latter

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* Dr. J. D. Cotton has confirmed that the rates recorded in Table 2 of ref. (*7*) are too large by a factor of 1000. The corrected rates are given in Fig. 10.

TABLE 2

ELOVICH CONSTANTS FOR HYDROGEN ADSORPTION ON NiO

Authors (ref.)	P_0 (mm Hg) T (°C) A ($m^2\ g^{-1}$)	β ($mole^{-1}\ m^2$)	α ($mole\ min^{-1}\ m^{-2}$)	Remarks
Charman, Dell, and Teale (*5*)	0.4 20 15.6[a]	5.5×10^{7}[a]	4×10^{-7}[a,b]	"Olive-green" oxide outgassed at 550°C
		5.8×10^{6}[c]	3.4×10^{-8}[c]	Oxygen preadsorbed at 400°C
		(3.4×10^{6})[d]	(3.0×10^{-8})[d]	Oxygen preadsorbed at 200°C
Cotton and Fensham (*7*)	0.037 22 145	3.6×10^{8}[e]	2×10^{-11}[e]	Black oxide, outgassed at 80°C
		(3.1×10^{7})[d]	(8.1×10^{-9})[d]	Black oxide, outgassed at 200°C

[a] Average value for two preparations of NiO.

[b] Using $t_0 = 2.7$ sec [estimated from Fig. 7 of ref. (*5*)].

[c] Calculated from linearized curve of Fig. 7, ref. (*5*), using $t_0 = 5$ min.

[d] Present work; β from Fig. 6 and α from the straight-line portion of Fig. 8.

[e] Calculated from an Elovich plot of the curve of Fig. 3 of ref. (*7*), using $t_0 = 150$ min.

applying to the results of Fig. 10). Such behavior, however, is not, within limits, incompatible with Elovich kinetics. Rates which fall to an approximately fixed value (see Fig. 3 of ref. *7*) can give reasonable Elovich plots provided the interval of "constant" rate is not unduly prolonged. With regard to rates which appear constant from zero time, the Elovich law may be written,

$$q = (1/\beta) \ln (1 + t/t_0)$$

For times which are small compared with t_0, the logarithmic factor simplifies to t/t_0, giving $q = t/\beta t_0 = \alpha t$. Thus the constant rate in such cases is identical with the initial Elovich rate and is less surprisingly found to have the same pressure dependence as the initial rates obtained in the present work.

The square-root pressure dependence has an important bearing on the interesting adsorption mechanism proposed by Cotton and Fensham (*7*). Briefly, hydrogen adsorption is considered to proceed in the following way [notation of Rees (*42*)],

$$H_2(g) + (Ni^{3+}/\square^{+})(\square_s^{+}) \rightleftharpoons H_2^{+}/\square_s^{+} + Ni^{2+}/\square^{+} \tag{6a}$$

$$H_2^{+}/\square_s^{+} + 2(O^{2-}/\square^{-}) \rightleftharpoons 2(OH^{-}/\square^{-}) + \square_s^{+} + e \tag{6b}$$

In order to account for the constant rate (and also for regeneration of the surface at 80°C without apparent desorption of hydrogen) it is proposed that H_2^+ or H^+, formed at the surface, diffuse toward the interior of the oxide grains. The excess oxygen being presumably immobile, a field then grows until the diffusion of H_2^+ or H^+ is exactly balanced by the diffusion of positive holes (Ni^{3+}) toward the surface. In such circumstances, a steady state will be set up at a given pressure, provided both sink and source (for hydrogen and positive holes, respectively) are sufficiently extensive. According to the pressure dependence, the rate process involves the atomic rather than the molecular species. Diffusion of H_2^+ may thus be rejected in favor of rate-controlling proton diffusion, the concentration of $OH^-/\square^-$ at the surface being governed by the gas pressure through (for example) the relatively fast reversible steps (6a) and (6b) above. It is conceivable that a detailed analysis of such a mechanism, corrected for the cumulative effects of finite sink and source, could account for Elovich kinetics. The mechanism suggests, in any case, that β should depend on the surface/volume ratio, increasing with the specific surface area of the oxide. It is unfortunately difficult to vary particle size, keeping all other factors constant.

If the mechanism of Cotton and Fensham is to be retained for adsorption on the black oxide, a different mechanism must be assumed for adsorption on the stoichiometric compound, where trivalent cations cannot intervene. The operation of two distinct mechanisms is, indeed, consistent with the results of Charman *et al.* (Table 2), where much larger values of α and β are obtained for the olive-green sample. It may be inquired whether the mechanism applicable to the latter continues to function, more or less independently, in the presence of excess oxygen. It can readily be shown graphically that, for the case of two Elovich processes such that the larger α is associated with the larger β, the Elovich plot for the sum must extrapolate to $P/P_0 < 1$ at $t = 0$, somewhat as shown in Fig. 3. With regard to the present work, it is possible that such an effect escaped observation in the absence of sufficiently precise data. However, if the values of α and β calculated from the results of Charman *et al.* for the olive-green oxide are assumed to apply to the yellow-green sample of the present work, then the nonlinearity of the Elovich plot at smaller times could scarcely have been missed. If the Elovich plots are indeed linear down to zero time, it may be concluded that the mechanism of adsorption on the stoichiometric compound becomes inoperative in the environment created by the presence of a sufficient excess of oxygen. It may be supposed, for example, that the excess oxygen has occupied the original hydrogen adsorption sites, or has served to empty surface (donor) levels which would otherwise have participated in hydrogen adsorption.

D. Interpretation of Elovich Kinetics

The results obtained for CO adsorption on the near-stoichiometric oxide (Fig. 2) may be considered to be in excellent agreement with the predictions of the Knudsen flow model.

The results obtained with the black oxide are rather fragmentary, but, added to those of Klier (*10*) (Fig. 2), suggest that the typical inverse pressure dependence is observed with the nonstoichiometric oxide as well. The values of β obtained, however, are only about 60% of those predicted by Eq. (4). This discrepancy has so far resisted analysis. All the evidence indicates that α is greater on the black than on the stoichiometric oxide, so that there is even more reason to expect rate-limiting diffusion with the former than with the latter. Values of β somewhat smaller than those predicted suggest that the "constant," a, increases during the course of the experiment. Such an effect may conceivably result from surface diffusion of adsorbed molecules (*43*), the contribution from which would rise with increasing coverage. There appears to be no reason to suppose, however, that the mobility of adsorbed CO is considerably greater on the black oxide than on the yellow-green.

A "catalytic" interpretation of the effect of excess oxygen on α has already been given. It may be supposed, in addition, that the greater negative surface charge due to the presence of excess oxygen will increase the mean diameter of the interparticle "pores." Such electrostatic effects are known to occur with fine oxide powders (*44*) and may partly account for the dependence of α on the excess oxygen content, since a is proportional to the fourth power of the mean pore radius.*

In the case of hydrogen adsorption, the Knudsen flow model, which might otherwise have accounted for the dependence of β on $1/P_0$, must be discarded for two reasons. Firstly, the observed values of β are only 45% of the theoretical ones and, secondly, the Elovich plots (Fig. 7) are linear down to zero time, in disagreement with the characteristic behavior of the Knudsen flow model for $P/P_0 < 0.8$ (Fig. 3). However, since the much slower CO adsorption is diffusion-controlled, it seems highly probable that the

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* Using the notation of Sutherland and Winfield (*32*), $a = (Y^2/t) = [3.76(\pi RT)^{3/2}/M^{1/2}V^2]k_e b^2 r^4$. Only k_e, b, and r are unknown. The Henry's Law constant, k_e, may be obtained from the isotherms of Fig. 1, of which the slope is close to unity, as required by the model (*32*). The number of pores, b, and the mean radius, r, can be estimated from the surface area, assuming uniform particle size (*45*, *46*). The approximate value of a thus obtained is in satisfactory agreement with the experimental results. It may be noted that the value of t_0 required to linearize the Elovich plot of data which satisfy Eq. (4) is $t_0 \simeq 0.04/a$. The slope of the foregoing plot is 0.35 ± 0.01, so that $\beta = 2.3ART/0.35VP_0$. Thus, $\alpha = 1/\beta t_0 = a(3.8VP_0/ART)$.

hydrogen adsorption rates were also limited by diffusion processes. It may again be supposed that surface diffusion contributes to the failure of the Sutherland and Winfield equation, but it must be concluded that no adequate interpretation of the hydrogen adsorption kinetics is available.

In the case of oxygen adsorption as well, the Knudsen flow model appears to be inadequate. The value of P/P_0 found by extrapolation of the linear plot to $t = 0$ is much too small (as little as 0.5 rather than 0.85) and the variation of β with P_0 indicated by Fig. 5 is much too pronounced. In view of the general behavior of the Elovich plots and of the values of β obtained, however, it cannot be excluded that the oxygen adsorption was at least partly diffusion-controlled.

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