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Adsorption upon Pure and Lithium-Doped Nickel Oxide

I. Oxygen

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The rate of adsorption of O_2 upon NiO + 0, 0.01, and 1.0 mole % Li_2O has been studied at constant pressure, about 10^{-1} mm, between −78° and about 400°C. Elovich kinetics are obeyed throughout, both log (rate) vs. θ and log $(t + t_0)$ vs. θ being linear; t_0 is always zero. The adsorptions obey the general equation

$$\text{Rate} = A_0P^x \exp(-m\theta) \exp(-E/RT)$$

Below the Néel point (T_N), $x = 0$ and E is small ($0\text{–}6\frac{1}{2} \pm 1\frac{1}{2}$ kcal mole^{-1}); above this temperature $x \sim 1$ and $E \sim 14$ to 18 ± 3 kcal mole^{-1} while m does not change much at the transition temperature. At the higher temperatures the chemisorption is accompanied by a very much slower incorporation into the lattice, which continues for many days. Isotopic experiments revealed that substantial desorption occurs while the adsorption is proceeding.

Addition of Li first decreased and then at 1.0 mole % Li_2O increased the initial rate of adsorption below T_N; above this temperature the main effect of Li is to increase the saturation coverage at constant pressure. In all cases the saturation coverage is minimal around 30–60°C, increasing at both lower and higher temperatures. O_2 is weakly chemisorbed in an uncharged molecular form, $O_{2(a)}$, below room temperature; above this increasing amounts of O_2^- are formed and above T_N the adsorbed species is mainly O^-.

It is suggested that adsorption occurs mainly along the exposed boundaries of the magnetic domains; below T_N the magnetostriction prevents the formation of 2 Ni^{3+} as nearest neighbors and so adsorption occurs as O_2^-, suitable sites being activated by the diffusion of P^+ away from them, this being the rate-limiting process. Above T_N the restriction on neighboring Ni^{3+} is removed and O_2 molecules possessing enough kinetic energy (14–18 kcal mole^{-1}) are chemisorbed as 2 O^-.

INTRODUCTION

There have been few detailed studies of the kinetics of O_2 adsorption on NiO, and none which have included lithium-doped materials and covered a wide temperature range. Most of the relevant literature has been summarized recently (*1*a,b).

Apart from its influence upon the conduction process at all temperatures, the nature of the adsorbed species at room temperature is of importance in the interpretation of calorimetric and infrared studies, including the reaction with CO, while as the temperature is raised interest shifts to the nature of the interaction between adsorbate and the oxygen ions of the lattice leading to place exchange, which has been studied by isotopic means (*19*). The band theory of electronic processes in solids does not apply to NiO as the conduction states are localized. This being so it is uncertain how far the concept of a Fermi surface and a Fermi level can be applied to discussions of adsorption and catalysis and it is of particular interest to examine how Li-doping effects the adsorption process in both depletive and cumulative chemisorption. The present work deals with

O_2. CO and CO_2 will be discussed in a later paper.

EXPERIMENTAL

Materials

NiO prepared from the nitrate and NiO containing 1.0 and 5.0 mole % Li_2O prepared by igniting the mixed nitrates, were from batches used in earlier studies (*2*); NiO + 0.01 mole % Li_2O was a fresh preparation. All samples contained about 85 ppm Na and 20 ppm K. Isotopically enriched and normal O_2 were prepared as before (*3*).

Adsorption Apparatus

The reaction vessel was of silica, connected by a graded seal through a U trap kept always at −78°C to a 4-mm tap and then to the remainder of the apparatus which was constructed of borosilicate glass; all connecting tubing was 6-mm ID. The reaction vessel was suspended vertically and was surrounded as required by a furnace or by a thermostat; the reaction vessel, trap, and connecting tubing to the tap had a volume of about 70 ml. The remainder of the adsorption volume comprised a Pirani gauge protected by a U trap at −78°C, and an associated constant-pressure device described fully elsewhere (*4*), by means of which the rate and amount of adsorption at constant pressure was automatically recorded. Further taps led to the gas dosing and sampling systems and to the pumps; the total adsorption volume was about 300 ml.

The gas dosing and sampling system was so arranged that an adsorption could be briefly interrupted and most of the gas rapidly replaced at the same pressure with gas of a different isotopic composition. It was also possible to isolate most of the gas phase from the adsorbent and rapidly recover it for subsequent isotopic analysis in a mass spectrometer. The system also included a small mercury vapor pump delivering into a calibrated volume and McLeod gauge on the high-pressure side so that accurately measured quantities of gas could be rapidly removed from the adsorption system and the adsorption continued with fresh gas after a known degree of desorption had been achieved.

Volume calibrations were performed using pure He.

Procedure

Adsorption kinetics. A number of preliminary runs (usually between 6 and 12) were necessary upon each sample before reasonable reproducibility was attained; it was in several cases necessary to carry out a further series of stabilizing runs when changing from one gas to another, as the work on O_2 was interspersed with similar work using CO and CO_2, which will be the subject of a separate communication. Before each run, both in the preliminary and in the main series, the sample was heated to 350–400°C while pumping; it was then exposed at that temperature to 1 cm of O_2 for 10 min, the gas pumped away for 3 min, and the O_2 treatment repeated. The oxide was then outgassed to about 1×10^{-6} mm for 2 hr at 500°C and then isolated and cooled to the adsorption temperature in 1 hr. After $\frac{1}{2}$ hr at the adsorption temperature the required dose of gas was added and the adsorption started by opening the tap between the adsorption vessel and the remainder of the adsorption volume. When the quantity adsorbed exceeded 100 ml at the operating pressure (this being the capacity of the rate-of-adsorption recorder) the adsorption was briefly interrupted, the recorder returned to zero, and a further increment of gas added. The standard pressure used throughout this work was 9×10^{-2} mm except for measurements of the effect of pressure on the rate of adsorption, where in general the pressure was varied between 4×10^{-2} and 2×10^{-1} mm.

We thus obtained a record of the volume of gas adsorbed (at constant pressure) versus time. From the tangents to the curves dq/dt was evaluated for various q and t and used for the Elovich plots discussed below.

Isotopic experiments. It was of importance to determine the degree of reversibility of the adsorption; the results are summarized in Table 3. The procedure adopted was to allow an adsorption using isotopically normal gas to proceed to a coverage θ_1 (based on the saturation coverage, θ_∞ at each temperature), then to isolate the adsorption bulb, pump out the remainder of the adsorption volume, and replace the gas so removed with the same quantity of gas of a different isotopic composition. The tap between the two sections was opened and the adsorption allowed to continue until it reached θ_2. At this point the adsorption bulb was again isolated and the gas in the remainder of the apparatus rapidly removed for analysis by mass spectrometer. The gas so removed was immediately replaced with more isotopically enriched gas and the adsorption allowed to proceed to θ_∞, at which point the residual gas was recovered and analyzed by mass spectrometer. All adsorption stages were as usual performed at a constant pressure of $\sim 10^{-1}$ mm.

Knowing the quantity of gas adsorbed at each stage and the dilution to be expected from the mixing of the gas spaces at each operation it was simple to calculate by stoichiometry from the isotopic analyses the amount x_1, of adsorbed gas, i.e., of θ_1, which had exchanged with the gas phase while the adsorption was proceeding from θ_1 to θ_2; x_2 similarly represents the additional amount of exchange between the adsorbed layer, θ_2, and the gas phase while going from θ_2 to θ_∞. These four quantities and Σx ($= x_1 + x_2$), together with Σx expressed as a percentage of θ_∞ are recorded in Table 3; also given is the percentage of the original adsorption exchanging while proceeding from θ_1 to θ_2, i.e., $100x_1/\theta_1$. The times for which the isotopically enriched gas was in contact with the surface, i.e., the time taken to proceed from θ_1 to θ_2, naturally varied with the speed of the adsorption but in all cases lay between 10 and 100 min; the enriched gas used between θ_2 and θ_∞ was normally left in contact overnight (~17 hr).

BET areas. These were determined using N_2 at $-193°C$; an area of 16.1 A^2 was assumed for the N_2 molecule.

Results

Stability of the Adsorbents: Reproducibility of Results

We have recently reported (*5*) that exposure of these oxide preparations to a large number of thermal cycles through the Néel point (~250°C) and/or to the gases CO, O_2, and CO_2 will in time bring about considerable increases in the surface area; typical changes found in the present work are shown in Table 1, taken from the earlier paper (*5*). It is to be noted that these changes were measured at the end of a long series of experiments embracing not only the work reported here but also a study of the chemisorption of CO and CO_2. Unfortunately this phenomenon was not noted until some time after the commencement of the present studies and figures are not available for some of the early work, notably the adsorption of O_2 on NiO. Since, however, we shall be concerned mainly with comparison of rates of adsorption at equal fractional coverages, based on the saturation coverage in each run, the fact that the surface has changed over a long period is not too serious. Also the experiments were performed in small groups with frequent calibrating runs under standard conditions to ensure that abrupt changes had not occurred, and that the activity of the solid remained sensibly constant.

TABLE 1
SURFACE AREA CHANGES

Sample	BET ($m^2 g^{-1}$) Original	Final	"Mean"	No. of runs
NiO	3.44	6.30	5	40
NiO + 0.01% Li_2O	8.96	12.1	10	90
NiO + 1.0% Li_2O	2.42	16.6	10	60

It was found that no advantage was gained by using liquid O_2 or N_2 in the trap protecting the adsorbent; solid CO_2 proved quite satisfactory in preventing contamination over periods of many months, judged by the repeatability of selected experiments.

The extent and rate of the adsorption were critically dependent on the precise outgassing and cooling technique used; this effect was most marked with O_2 at the lower adsorption temperatures. Thus, with O_2 on NiO + 1.0 mole % Li_2O, if the oxide, after the usual outgassing at 500°C, was kept isolated for 24 hr at 106°C before adding the O_2, the adsorption started at a rate ~1/2000 that obtained by the standard technique. Instead of the rate falling rapidly as coverage increased, i.e., according to Eq. (7) (below), it fell only slowly according to Rate $\propto \exp(-3.7\theta)$; thus it fell to 1/6 of the initial value at $\theta = 0.5$; the saturation coverage was also reduced by 37%. (The effect was not so pronounced on pure NiO.)

Adsorption

Kinetics

On all four powders the adsorption of O_2 at all temperatures between room temperature and roughly 450°C consisted of an initial more or less rapid stage, an activated chemisorption, followed at the higher temperatures by a much slower adsorption, due to the slow incorporation of O_2 as O^{2-} into the solid, which continued for a long time. The completion of the first process was taken to be when there was no further uptake in 3 hr; this point was always fairly sharply defined and usually occurred within the first 12 hr. This criterion defines the terms θ_∞ or equilibrium coverage throughout this paper. The initial chemisorption forms the main subject of the present study and followed Elovich kinetics throughout, plots of both $\log(dq/dt)$ vs. q and of $\log(t + t_0)$ vs. q being linear; in all cases we found $t_0 = 0$, although it must be noted that usually the initial rate was not measured (see below).

The slow incorporation process has been followed for up to 160 hr between 250° and 400°C without showing signs of saturation. On NiO the rate yielded an activation energy of ~3 kcal mole^{-1}; on the other solids it was less reproducible but also possessed only a small or zero activation energy. On NiO it had a velocity at 300°C of roughly 5–15 × 10^{-4} ml (NTP) g^{-1} per 12 hr; corresponding figures for NiO + 0.01 mole % Li_2O and 1.0 mole % Li_2O are 10–20 × 10^{-4} and 150–200 × 10^{-4}, respectively.

We do not find it possible to separate the initial chemisorption on our "aged" materials into three processes as do Charman *et al.* (*1*a). In particular we do not observe inflections in the q vs. $\ln(t)$ plots, both these and the log (rate) vs. q plots being fairly accurately linear throughout, even in the preliminary runs. We have, however, not concerned ourselves with any rapid initial adsorption occurring at a speed greater than that of the recording device, namely about 1 ml sec^{-1}; this occurred in most experiments and amounted to between 5% and 30% of the total adsorption. The results for the various adsorbents are summarized in the following sections.

NiO

(a) ~420° to ~250°C. Rate $\propto P_{O_2}^{1.0}$ from $\theta = 0.3$ to 0.9 over the range 5×10^{-2} to 2×10^{-1} mm. Rate at constant pressure falls with increasing θ; activation energy constant between $\theta = 0.3$ and 0.9 at 18 ± 3 kcal mole^{-1}. The rate of adsorption obeys the relationship

$$\text{Rate} = A_0 P \exp(-m\theta) \exp(-E/RT) \quad (1)$$

Expressing the rate as ml (NTP) g^{-1} min^{-1} then with P in mm the values of the constants are

$$A_0 = 2.75 \times 10\,\text{ml(NTP)}\,g^{-1}\,\text{min}^{-1}$$
$$m = 9.2$$

when E equals 18 kcal mole^{-1}. In this equation θ is the fraction of the saturation coverage θ_∞; at these temperatures and pressures θ_∞ is at the most only some 3% of the monolayer capacity. The restriction of Eq. (1) to the range $\theta = 0.3$ to 0.9 is necessary since the rates of adsorption were too fast to measure below about $\theta = 0.25$, while above $\theta = 0.9$ the rates became too slow for accurate measurement.

It is of interest to record that essentially the same values for the constants of Eq. (1) were obtained upon a series of experiments (using another sample of the same batch of NiO) in which the oxide was outgassed for 18 hr at 500°C between runs.

(b) ~250° to ~30°C.

$$\text{Rate} = A_0 \exp(-m\theta) \exp(-E/RT) \quad (2)$$

with

$$A_0 = 5.7\,\text{ml(NTP)}\,\text{g}^{-1}\,\text{min}^{-1}$$
$$m = 7.6$$
$$E = 6\tfrac{1}{2}\,\text{kcal mole}^{-1}$$

with the same restriction of P and θ as in (1); the estimated error in E is $\pm 1\frac{1}{2}$ kcal mole^{-1}.

(c) Below ~30°C. Between 30° and about 0°C the rates of adsorption at various θ's remain roughly constant at the values reached at the lower end of the second range: $E \sim 0$. Between ~0° and −78°C the rate increased very rapidly, so that at −78° the rates are 10^3 faster than at 0°C. The influence of gas pressure upon the rate has not been measured below 30°C.

(d) Equilibrium coverage. The quantity of O_2 adsorbed at equilibrium at a constant pressure of 9×10^{-2} mm rises roughly linearly from about 50×10^{-4} ml NTP g^{-1} at 0°C to $\sim 300 \times 10^{-4}$ at 300°C, remaining at this figure to the highest temperature of observation 425°C. The equilibrium quantity increased again below 0°C reaching about 90×10^{-4} ml NTP g^{-1} at −78°C.

NiO + 0.01% Li_2O

The kinetics are very similar to those found on the pure oxide, the main differences being that as the temperature was reduced the rates began to increase with decreasing temperature at about 60°C instead of 0°C, and the change in E at higher temperatures occurs around 200°C. In general the observations covered the range $\theta = 0.1$ to 0.9.

(a) ~320° to ~200°C.

$$\text{Rate} = 4.1 \times 10^5 P^{0.8} \exp(-4.8\theta) \exp(-18000/RT) \quad (3)$$

The estimated uncertainty in E is ± 3 kcals mole^{-1}.

(b) ~200° to 60°C.

$$\text{Rate} = 4.1 \times 10^{-4} \exp(-3.4\theta) \exp(-500/RT) \quad (4)$$

the estimated error in E being ± 1.5 kcal mole^{-1}.

(c) Below 60°C. There is no region corresponding to that described under (c) for NiO, (b) and (c) being apparently merged into one. The quantity adsorbed, and the rate of adsorption again both increase markedly at −78°C.

(d) Equilibrium coverage. The equilibrium coverage of O_2 at 9×10^{-2} mm showed rather more scatter than with NiO, but again rises roughly linearly from $\sim 100 \times 10^{-4}$ ml (NTP) g^{-1} at 20° to $\sim 500 \times 10^{-4}$ at 300°C.

A further series of experiments with O_2 after this sample had been used to study the adsorption of CO and CO_2 showed very little departure from Eqs. (3) and (4).

NiO + 1.0% Li_2O

This material showed the greatest change of BET area during the course of a series of experiments (see Table 1) and this lability was reflected in changes in the kinetics of adsorption in the high-temperature range; a similar comparison of fresh and aged material was not carried out below 250°C.

(a) 420° to ~250°C. The first 20 experiments yielded the equation

$$\text{Rate} = 1.2 \times 10^{10} P^{1-\frac{1}{2}\theta} \exp(-19.2\theta) \exp[-(23 - 8\theta)1000/RT] \quad (5)$$

But after some 20 further runs, which included those under (b), this had changed to

$$\text{Rate} = 1.1 \times 10^6 P^{0.85} \exp(-11\theta) \exp(-14\,000/RT) \quad (6)$$

Equation (6) was substantially unchanged by outgassing the sample for 18 hr instead of the usual 2 hr. The uncertainty in the E terms are again ± 3 kcal mole^{-1}.

The experiments leading to the pressure exponent in Eq. (5) were performed in random order in triplicate over the pressure range 5×10^{-2} to 2×10^{-1} mm, good agreement being found between replicates. From the plots of log (Rate) vs. log (pressure) the exponent n in the equation

$$\text{Rate} \propto p^n$$

was evaluated for various θ between 0.4 and 0.9.

(b) 250° to ~60°C.

$$\text{Rate} = 2.8 \times 10^{-1} \exp(-10.3\theta) \quad (7)$$

(c) Below 60°C. No detailed study of this region was carried out but it was confirmed that on this material also both the quantity and speed of adsorption increased markedly again at −78°C.

(d) **Equilibrium coverage.** The equilibrium coverage with O_2 over the first 20 runs at 9 × 10^{-2} mm remained constant at 450 ± 50 × 10^{-4} ml (NTP) g^{-1} from 25° to ~160°C, then rose roughly linearly to about 1300 × 10^{-4} ml (NTP) g^{-1} at ~350°C and thereafter decreased slowly to ~1100 × 10^{-4} ml at 450°C. The adsorption during later runs, by which time the BET area had undoubtedly increased, and when Eq. (6) was operative, was some 10% less than the above.

NiO + 5.0% Li_2O

A detailed study has not been made with this material but it has been confirmed that it exhibits the same general features as the others. The adsorption above ~190°C has an activation energy of more than 10 kcal $mole^{-1}$ and is pressure-dependent; between 190°C and room temperature the activation energy is roughly nil, and the process is independent of P_{O_2}.

DISCUSSION

A. Magnetic and Electric Properties

We consider the most important of our findings to be the change in the nature of the chemisorption with O_2 which occurs around 200–250°C. The Néel point (T_N) for pure NiO of about the same particle size as that used here is about 247°C (*12*a, *35*) and by analogy with the very similar Li–Co–O system (*12*b) would be expected to fall with addition of increasing amounts of Li. The change is from an antiferromagnetic to a paramagnetic state; a small amount of ferrimagnetism in the presence of O_2 due possibly to super-exchange coupling between rows of Ni^{3+} has been reported (*13*) in Li-doped NiO. The possible importance of the magnetic structure of NiO catalysts in determining the reactivity has not so far attracted much attention except for a brief mention by Parravano and Boudart and by Bielanski and Haber and papers by Cimino *et al.* and Mehandjiev and Bliznakov (*14*). Thus Charman, Dell and Teale (*1*a) and Kutseva and Keier (*18*) found that a change occurs in the mechanism of O_2 adsorption around 250°C but failed to notice the possible significance of this temperature. Similarly, a change in the kinetics of adsorption between 200° and 300°C was reported by Engell and Hauffe (*15*). By a combination of X-ray, optical, and neutron diffraction techniques (*16*) it has been established that, even in single crystals of NiO, the antiferromagnetic state comprises a large number of domains in each of which the spins of alternate layers of Ni^{2+} ions are aligned parallel to each other. The crystal thus exists in a multispin axis stage below the Néel temperature. Due to the magnetostriction each domain is slightly distorted from the rocksalt structure which occurs above the transition temperature; the symmetry in the antiferromagnetic state is rhombohedral, the distortion from the cubic form being some 6′ of arc in 90°. The boundaries between the domains are either T (twin) or S (spin reversal) in type: Both are associated with point defects in the lattice. Temperature cycling through the Néel point leads to the formation and destruction of the domains with the associated stressing and relaxation of the lattice. The positions of the domain boundaries in single crystals are very easily changed by this means and they are also readily moved by small mechanical stresses or magnetic fields (*16*b). The more nearly perfect crystal lattice above the transition temperature is more resistant to deformation and accordingly the Young's modulus of a sintered bar of NiO increases (*17*) by ~60% as the temperature is raised through the Néel point; a similar change occurs with CoO.

The conductivity of NiO is thought to be due to the movement of self-trapped positive holes (*12*b, *18*), there being no *d* band owing to the lack of overlap of the 3*d* orbitals of the nickel ions, and the associated activation energy is accordingly that required to release the lattice distortion. This also changes from ~11½ kcal $mole^{-1}$ below 250°C to ~23 kcal $mole^{-1}$ at higher temperatures (*18*). We have confirmed that our sample of NiO exhibits this change in activation energy (*10*). The mobility of the holes is small, estimated as between 2 and 60 × 10^{-5} $cm^2\ V^{-1}\ sec^{-1}$ at room temperature and this accounts for the lack of any measurable Hall effect (*18*).

B. Interaction of the Surface with O_2

From a consideration of the enthalpy changes of gas-phase reactions involving oxygen species (*19*) we concluded that the most likely species first formed on the chemisorption of oxygen is O_2^- followed by 2 O^-; the direct formation of 2 O^{2-} was shown to be most unlikely. The present results are in agreement with these conclusions. On our preparation of NiO, suitably aged, we suggest that at low temperatures, say from around room temperature to below −78°C, O_2 is adsorbed as molecules mainly in a loose type of chemisorption, $O_{2(a)}$, which does not involve electron sharing; possibly, owing to the order existing in the spins of the Ni^{2+} in the solid, the interaction involves the spin of the unpaired electrons in the oxygen molecule. This adsorption is readily reversible, as is shown by the first experiment in Table 3.

As the temperature is raised the $O_{2(a)}$ is desorbed and between roughly room temperature and 250°C, oxygen is readsorbed mainly as O_2^- by a mechanism which is limited by a process occurring in the solid [since from Eq. (2) the rate is not dependent upon P_{O_2}], almost certainly the movement of conducting species through the surface; very probably this is the migration of P^+ away from the immediate neighborhood of an otherwise suitable adsorption site, thus "unlocking" it for the adsorption process. This is the process described by Eqs. (2), (4), and (7). The adsorption of O_2^- is also largely reversible but less easily than that of $O_{2(a)}$ (cf. Table 3). We propose that this adsorption, and the conducting process, can occur only along the boundaries of the magnetic domains (which include, of course, the physical boundaries, edges and corners, of the particles themselves) where almost certainly most of the crystalline defects and impurities will be concentrated. Suitably exposed Ni^{2+} ions will occur where these boundaries emerge at the surface. It is probable that some of the O_2^- will be converted to O^- on long residence in the surface or as the temperature is raised but this is a secondary process which does not affect the kinetics until the Néel point is reached. This conversion may be the reason why $x_1/\theta_1 > \Sigma x/\theta_\infty$ in Table 3 between room temperature and ~100°C. O^- is probably the species responsible for Gossel's observation (*20*) that a stable charged form of excess oxygen distinct from the lattice O^{2-} exists on NiO (prepared from the carbonate) for long periods below 100°C.

It is to be understood that where we write an adsorbed species as O_2^- or O^-, etc., we do not necessarily imply full transfer of an electron; as we have commented elsewhere, the degree of transfer is still largely unknown, but the symbols O_2^-, O^-, etc., remain a useful shorthand (*19*).

We think that above ~250°C the release of the magnetic restraints in the lattice permits the more general existence of positive holes on neighboring Ni ions, and O_2 molecules approaching single exposed Ni^{2+} with the correct orientation and excess energy (~18 kcal mole^{-1}) are adsorbed according to Eqs. (1), (3), and (6) forming 2 O^-. We do not consider that the presence of two neighboring exposed Ni^{2+} ions is necessarily required as no abrupt change in the coverage occurs at 247°C; we associate the activation energy with the energy needed to force the formation of a second positive hole, located on a neighboring, probably shielded, Ni^{2+}. The energy involved may be of the same order as, but probably rather less than, that needed in the bulk conduction process to release the self-trapped positive holes. An oxygen molecule approaching an activated site with the correct orientation but possessing less than this amount of kinetic energy may be adsorbed as O_2^- but will, we suggest, be almost immediately desorbed and so contribute nothing to the adsorption kinetics.

As the temperature is raised above 250°C an increasing number of the O^- will exchange electrons with neighboring O^{2-} of the lattice. Since the adsorption of O^- is at least partly reversible (cf. Table 3) this charge exchange of oxygen could cause the migration of the adsorption sites across the surface and so account for the general isotopic exchange between gaseous O^{18}-enriched oxygen and the whole surface lattice layer of O^{2-} which is observed (*19*) at these temperatures. However, we prefer to regard the adsorption sites as relatively immobile and consider the O^- as the mobile species at higher temperatures. The quasiliquid nature of the surface layers accounts also for the very slow incorporation of oxygen which is found at the higher temperatures. We think that neither this charge exchange, nor the accompanying place exchange leading to O exchange has any effect on the kinetics of oxygen chemisorption in this temperature range.

Thus, below ~250°C we write the adsorption–desorption reaction

$$(\mathrm{C})(\square_s^+/\mathrm{Ni}^{2+})(\square_s^-) + \mathrm{O}_{2(g)} \rightleftharpoons (\mathrm{C})(\square_s^+/\mathrm{Ni}^{3+})(\square_s^-/\mathrm{O}_2^-) \quad (8)$$

and above 250°

$$(\mathrm{C})(\square_s^+/\mathrm{Ni}^{2+})_2(\square_s^-)_2 + \mathrm{O}_{2(g)} \rightleftharpoons (\mathrm{C})(\square_s^+/\mathrm{Ni}^{3+})_2 + 2(\square_s^-/\mathrm{O}^-) \quad (9)$$

followed by

$$(\square_s^-/\mathrm{O}^{18-}) + (\square_s^-/\mathrm{O}^{16\ 2-}) \rightleftharpoons (\square_s^-/\mathrm{O}^{16-}) + (\square_s^-/\mathrm{O}^{18\ 2-}) \quad (10)$$

The prefix (C) denotes a surface complex (including perhaps the presence of several aggregated defects in the surface or immediate subsurface layers) with the correct geometry for an adsorption site.

We have shown elsewhere (*2*) that the rate of *desorption* of O_2 is increased by a factor of ~10^3 at 1.0 and 5 mole % Li_2O above 200–250°C and leads to significant increases in the rate of N_2O decomposition (*2*, *14*) and in the rate of O^{18} exchange between O_2 gas and the surface between ~200° and 500°C (*2*): This illustrates the influence of the lithium level on the reversal of Eq. (9), due at least in part to the increase in P^+; the dependence is greater than to the first power of the lithium concentration. The proposed model, in which the adsorption sites (even above the Néel temperature) are concentrated along the domain boundaries, accounts for the small degree of coverage found, bearing in mind that our θ_∞ is at most only a few per cent of the whole surface. Concentration of the conducting paths also along the domain boundaries is also suggested by the fact that ~1% coverage of the whole surface of our NiO by oxygen causes a large drop in the specific resistance at 300°C (*10*). Morin (*22*) has reported "grain boundary" conduction in NiO prepared at 1100–1200°C and cooled in an atmosphere of oxygen; the material prepared and kept in a slightly reducing atmosphere was free from this effect.

The solid may thus be regarded as an assembly of quasiperfect crystalline zones, which below 250°C form the magnetic domains, almost free from impurities and defects and of very low electrical conductivity; the exposed faces of these zones will have low reactivity towards gases. Defects, impurities, conducting paths, and sites of gas adsorption and catalytic activity are concentrated along the boundaries of the zones.

Charman *et al.* (*1*a) have proposed the formation of O_2^- and O^- upon NiO but they differ from us in thinking that the adsorption at low temperatures is O_2^- and not the uncharged species; similarly they regard the adsorption at room temperature as mainly O^- and not O_2^- and at higher temperatures as O^{2-} rather than O^-. We have found that the isotopic equilibration reaction between $O^{16}{}_2$ and $O^{18}{}_2$ is catalyzed by NiO and by the doped materials used here and that it occurs at the same temperatures, ~250°C and upwards, and at the same speed as the general isotopic exchange with the surface (*2*); this has recently been confirmed for NiO by Boreskov *et al.* (*11*). The conclusion has been drawn from this by Charman *et al.* (*1*a) that the room temperature chemisorption of oxygen on NiO occurs as O^-—this extrapolation to lower temperatures is not justified. In the course of the present work we have put ~500 ml at 10^{-1} mm of nonequilibrated $O^{16}{}_2 + O^{18}{}_2$ in contact with 1 g of NiO (both a freshly prepared and an "aged" sample were examined) at 20°C for 24 hours with no detectable equilibration nor any exchange with the surface although (Table 3) a substantial degree of desorption occurs during the adsorption. Our earlier observations are entirely in accord with our present results and conclusions, that reversible dissociative chemisorption of oxygen on NiO of relatively coarse particle size prepared from the nitrate or carbonate, does not occur appreciably below the Néel temperature. It is, of course, possible that around room temperature O_2 is chemisorbed as 2 O^- upon isolated pairs of sites so that when desorption occurs no mixing of atoms from different molecules takes place, and hence no equilibration nor any O^{18} exchange with the surface is observed. This we regard as unlikely since the formation of O^{16-} on NiO^{18} surfaces is in our experience always accompanied by isotopic exchange with the surface [Eq. (10) above], e.g., during the decomposition of N_2O between room temperature (*10*) and 200–300°C (*2*).

C. *Kinetics*

The significance of the experimental equations [(1)–(7)] and of the observed apparent adherence to Rojinsky-Zeldovitch-Elovich (RZE) kinetics requires some comment. In the first place the saturation coverage at constant pressure varied over the whole temperature range, and in addition the kinetics recorded (and therefore the values of the quantities m, A_0, E, and the exponent of P) are the net result of adsorption and a simultaneous desorption (cf. Table 3). Detailed quantitative conclusions and comparisons are therefore unwise; the various equations serve as useful semiquantitative comparisons of the properties *of this series of preparations of doped oxides* while it is clear that a change of mechanism occurs around the Néel temperature. Thus our model would require that E in Eqs. (2), (4), and (7), i.e., $6\frac{1}{2}$ to 0 kcal mole^{-1} to be roughly that found from semiconductivity measurements on the same materials [$E_\sigma = 11 - 2$ kcal mole^{-1} (*10*); cf. also ref. (*18*)]. Above T_N a similar relationship should be found and indeed the value of roughly 18 kcal mole^{-1} [Eqs. (1) and (3)] is very close to E_σ for these two materials *in vacuo* (*2*). For the oxide containing 1.0 mole % Li_2O, however, E_σ *in vacuo* is ~2 kcal mole^{-1} (*2*) compared with the value of ~14 kcal mole^{-1} [Eqs. (5) and (6)]. It is, however, probable that our earlier conductivity measurements, being DC, relate only to the surface conducting states and that the material containing 1 mole % Li_2O retained sufficient excess oxygen in the surface to short-circuit the bulk conductivity, whereas with the other two materials sufficient outgassing was achieved to give a close approximation to the bulk figure. Other workers (*12*b) have recorded values of 28 for pure NiO falling to ~7 kcal mole^{-1} for material containing 1.0 mole % Li_2O by DC measurements in the absence of O_2; AC has given ~39 and 16 kcal mole^{-1} (*21*) in air upon well-sintered specimens, so that there are grounds for believing our figure of 2 kcal mole^{-1} to be too small.

The values of m found by us are larger than would be expected from statistical considerations for our model of the surface. Thus at pressure P the rate of condensation of a diatomic molecule occupying two sites into an immobile film without interaction between the adsorbed species is (*23*)

$$\frac{d\theta}{dt} = \frac{2z\alpha P}{n_s(2\pi mkT)^{1/2}} \frac{(1-\theta)^2}{z-\theta} \quad (11)$$

where z is the number of nearest neighbors; n_s, the number of sites per unit area; m, the molecular weight; and α, the condensation coefficient; z is usually 4 or 6 but could be 2 if adsorption occurs into a linear array such as might be involved in domain boundary adsorption.

Considering only the variation of the rate with θ assuming all other terms constant we have, with θ small

$$\ln(d\theta/dt) = \text{const.} - \theta[2 - (1/z)] - \text{higher powers of } \theta \quad (12)$$

where the coefficient of θ, $[2 - (1/z)]$ is to be compared with those given by Eqs. (1), (3), (5), and (6), namely, 9.2, 4.8, 19.2, and 11.0. Clearly no value of z will fit our results: in the case of adsorption into a mobile film without interaction, the corresponding coefficient of θ becomes 2. The discrepancy cannot be removed by the inclusion of a repulsion energy term, $e^{-n/kT}$, in the statistics, since this would mean that our m should vary with temperature, contrary to our observations. Now the fact that an adsorption obeys RZE kinetics has almost always been taken to imply that the surface consists of a semi-infinite number of sets of sites of different adsorption potential; this cannot be true here because of the lack of change of the activation energy of adsorption with coverage. We have recently (*24*) demonstrated, however, that a very small number of sets of sites is all that is necessary. Thus, by assuming, for example, five sets, each containing the same number of sites, and the adsorption on each set following the law

$$d\theta_j/dt = k_j(1 - \theta_j) \qquad (13)$$

satisfactory RZE plots are obtained with the k's in the ratio $e{:}e/5{:}e/30{:}e/160{:}e/1000$ (Fig. 3 of ref. *24*). In this case the value of m from the plot of log (Rate) vs. θ is 9.2, exactly the same as that found by us for NiO [Eq. (1)]. We have also shown that this simplified model will allow some desorption the effect of which, if desorption is an activated process, can be to cause sets of sites to drop out as the temperature is raised, and for new sets to become active.

Our observations appear to be adequately explained by a model surface containing possibly as few as three to five sets of sites in a limited temperature range, although it is likely that rather more are involved over the interval ~30° – 350°C. For each oxide m is roughly the same throughout this temperature range despite the change of mechanism at the Néel point, and, as shown by the saturation coverage, the number of sites increases slowly with temperature, coupled with increasing desorption (Table 3). We conclude that sets of sites do become kinetically unimportant as the temperature is raised, but this is not a discontinuous process, the ratios between the various θ_j changing only slowly; an abrupt change in the temperature dependence of the k_j alone occurring at T_N.

In order to compare Eqs. (1) to (7) it is convenient to tabulate the rates of adsorption at $\theta = 0$ and $\theta = 0.5$ calculated from these equations at a temperature in the middle of the range. This is done in Table 2 using a temperature of 667°K ($10^5/T = 150$) for Eqs. (1), (3), (5), and (6) and 400°K ($10^5/T = 250$) for Eqs. (2), (4), and (7). The first entry under 667°K for the 1.0% Li_2O material refers to Eq. (5) and the second to Eq. (6). Assuming that the saturation coverage in molecules per gram at 10^{-1} mm is equal to the number of adsorption sites we may calculate the initial rate of adsorption, R_s, molecules per site per minute; these values are given for the two temperatures in the fourth and seventh columns of Table 2. R_s has no great significance except for purposes of comparison since we do not consider that more than one molecule is adsorbed per site and also the rates fall off very rapidly as the coverage is increased. The adsorption is in any case very slow; if we assume each adsorption site has an active area of 10 Å^2, the rate of bombardment, molecules min^{-1} at 10^{-1} mm, per site is 1.4×10^6 at 667°K and 1.7×10^6 at 450°K, which compared with the values for R_s in Table 2 indicate very low values for the adsorption coefficient, in agreement with the approximate values already derived indirectly for these oxides (*2*). [It may be remarked here that the figures in Table 2 are not inconsistent with the rates of O^{18} exchange between O_2 gas at 3.4 cm and the O^{2-} in the oxide surface which have been reported elsewhere (*2*), if it is assumed that the rate of adsorption continues to increase with pressure over this range.]

It is evident that although there are some differences of detail, the main effect of Li

TABLE 2

RATE OF ADSORPTION OF O_2[a]

Li_2O (mole %)	400°K			667°K		
	$\theta = 0$	$\theta = 0.5$	R_s[b]	$\theta = 0$	$\theta = 0.5$	R_s[b]
Nil	1.7×10^{-3}	3.8×10^{-5}	1.4×10^{-1}	4.1×10^{-1}	4.1×10^{-3}	14
0.01	2.2×10^{-4}	3.9×10^{-5}	10^{-2}	10^{-1}	8.7×10^{-3}	2
1.0	2.8×10^{-1}	1.6×10^{-3}	6	5.3×10^{-1}	9.4×10^{-2}	4.4
	—	—	—	1.2×10^{-1}	1.7×10^{-2}	1.1

[a] In ml (NTP) g^{-1} min^{-1}.

[b] Molecules per site per minute: see text.

doping in the high-temperature region (apart from the profound effect on the rate of oxygen desorption mentioned above) is to increase the amount of O_2 adsorbed at saturation at $\sim 10^{-1}$ mm. This effect of Li upon the saturation coverage is also evident at higher pressures; thus at 3.4 cm and 450°C the corresponding figures (*10*) are 480×10^{-4}, 550×10^{-4}, and 1540×10^{-4} ml (NTP) g^{-1} upon, respectively, NiO containing 0, 0.01, and 1.0 mole % Li_2O; these figures refer to fresh unaged samples with BET areas given in the second column of Table 1. Similar results were found in an earlier study (*2*). The initial *rates* of adsorption per gram at $\sim 10^{-1}$ mm are virtually unaffected in the higher temperature range, while at lower temperatures the rate is first decreased and then increased by Li additions. On the other hand the initial rates of adsorption per active site, R_s, although they change in a similar manner to the rates per gram in the lower temperature range, indicate a rather faster rate at higher temperatures on pure NiO than on either of the other powders. The lower reactivity of NiO + 0.01 mole % Li_2O below 250°C may be due to the destruction of positive holes and the filling of Schottky cation vacancies in pure NiO containing excess oxygen on the addition of small amounts of Li, as was first suggested by Brownlee and Mitchell (*6*) [cf. also Parravano (*7*)]. This could well affect the configuration of the defect aggregations responsible for the adsorption–desorption sites [see Eqs. (8) and (9)].

Kutseva and Keier (*8*) have also reported only a slight fall in E for the adsorption of O_2 as the Li content of NiO is increased; they also record an increase in the saturation coverage in the region 200–360° at 0.8 atom % Li and state that the activation energies in the regions 200–250°C and 310–360°C are not the same.

Table 3 shows clearly that even while RZE kinetics are being obeyed by the net adsorption rates, a substantial amount of desorption is occurring. The extent ($100\Sigma x/\theta_\infty$) of the desorption does not differ greatly over the three oxides in the temperature range studied here but shows, as would be expected, a distinct increase as the temperature is raised: The one experiment above 300°C, on NiO, exhibits the beginning of the general isotopic exchange reaction between the surface O^{2-} ions and the gaseous O_2. The experiments summarized in this table were performed on the "aged" oxides during the course of the main kinetic investigation but a few experiments upon fresh samples of these oxides gave very similar results.

Charman Dell and Teale (*1*a) studied the reversibility of the adsorption by pumping at the adsorption temperature and found

TABLE 3

EXPERIMENTS USING O_2 ENRICHED IN O^{18}

Li_2O (mole %)	T (°C)	Ml (NTP) per g × 10^4						$\frac{100\Sigma x}{\theta_\infty}$	$\frac{100 x_1}{\theta_1}$
		θ_1	θ_2	θ_∞	x_1	x_2	Σx		
Nil	−78[a]	8	17	113	8	100	108	96	100
	20	10	23	46	7	9.5	16.5	36	70
	24	15	23	47	10	—	—	—	67
	86	20	38	63	7.3	10.7	18	29	36
	324	206	271	320	591	2040	2631	822	287
0.01	22[b]	32.4	60.6	154	28	70	98	64	87
	48[c]	42.2	63.8	146	32	35	67	46	76
	90	30.2	47.6	97	19	46	65	67	63
	206	208	354	580	46	390	436	75	22
1.0	106	—	264	382	—	—	146	38	—
	245	—	200	441	—	—	316	72	—

[a] The experiment at −78° was performed in duplicate: close agreement was found.

[b] 1.2% O^{18} used: 9.0% O^{18} used in the other runs.

[c] Sample outgassed for 18 hr at 500°C; remainder outgassed for 2 hr at 500°C.

that ~50% of the total adsorption at ~0.03 mm was desorbed in 2 hr at room temperature and none at 100° and above. The room-temperature fraction is a little more than we find by isotopic means but it is probable that their adsorptions were not allowed to proceed to completion. We find that between room temperature and ~250°C roughly half as much of the O_2 adsorbed in the first 1–2 hr is desorbed by pumping at the adsorption temperature for 17 hr as is revealed as being reversibly adsorbed by the isotopic technique (x_1 of Table 3) during a contact time of ~$\frac{1}{2}$–1 hr. We have also found that at room temperature the amount of desorption from a saturated surface after 18 hr pumping is rather less than half the values of Σx given in Table 3. Similarly at −78°C on NiO, 46% of the O_2 adsorbed in the first 60 min is recovered on pumping at that temperature for $\frac{1}{2}$ hr compared with 100% reversibility by the isotopic method. We prefer the isotopic technique as it must give a better measure of the true reversibility of the adsorption.

D. Lability of the Surface

The lability of the surface of the adsorbents is shown by the surface area changes (Table 1), by the way in which activity of a freshly outgassed surface can be partly annealed away by maintaining it for some hours *in vacuo* at the adsorption temperature (at least when this is 100°C or more) prior to commencing the adsorption, and by the exchange of O^{18} between enriched gas and the surface. With O_2 it is difficult to be sure at what temperature exchange between gas and lattice commences, because it is not possible to remove for certain all the excess oxygen from the surface of NiO; addition of Li_2O results in the retention of more oxygen. A recent study (*9*) has shown the presence of considerable amounts of excess oxygen, after outgassing, in the bulk lattice of NiO containing Li. Pure NiO made by calcining the basic carbonate was free from excess oxygen but the NiO used in the present study, made from the nitrate, retains appreciable, but variable, amounts of O_2 in the interior after outgassing for 16 hr at 550°C (*10*). This oxygen probably slowly diffuses outwards to the surface, making it impossible to prepare truly oxygen-free surfaces [cf. also ref (*1*a)]. It is, however, quite certain that between 200° and 300°C oxygen exchange sets in between the gas and virtually the whole of the O^{2-} in the oxide surface with all the materials used here (*2*). Our earlier work upon oxygen exchange with NiO has recently been confirmed by Russian workers (*11*).

Faced with this well-established lability of the surfaces we wished to study we could either use a fresh sample for each run or do our best to standardize conditions and introduce checks for reproducibility at frequent intervals. In view of the extent of the work planned we have chosen the second alternative. We also believe that our procedure has lead to the destruction of abnormally active sites which might be a cause of irreproducibility or might confuse the general kinetic picture. For example, we did not encounter the inflections in the plots of q vs. ln $(t + t_0)$ found by Charman *et al.* (*1*a) at small values of t. We consider it, even so, unlikely that the preexponential terms, A_0, in our various rate expressions [Eqs. (1) to (7)], are very accurate—neglecting the effect of the uncertainty in E the quoted values of A_0 might differ by a factor of 2 to 4 on a fresh sample. It is also regrettable that because of the surface area changes it is not possible to refer either the A_0 or the observed rates of adsorption to unit areas of the catalyst with any great certainty. In this paper we have assumed the "mean" areas given in the fourth column of Table 1. We have found, however, by a few experiments on "aged" samples of fresh preparations of NiO and of NiO + 0.01 mole % Li_2O that E and M are not significantly different from those reported here. Continuous use of the same sample, coupled with frequent thermal cycling through the Néel point, may be expected to promote alterations in the surface by favoring the concentration, by slow migration, of defects and impurities in the magnetic domain boundaries.

The relative importance of the possible reactions is sometimes significantly changed by repeated use of the solid, as is shown by the finding that Eq. (5) changed to Eq. (6) on continued use of the 1.0% Li_2O material. Equation (5) would imply that the formation of 2 O^- required some 9 kcal more on the young material than on the aged. Also that at first there were very few places where 2 O^- could be accommodated as pairs on neighboring sites, so that the process rapidly became limited by diffusion of one of the O atoms, either as O or O^- to more distant sites. This model accounts for the term $P^{1-\frac{1}{2}\theta}$ in Eq. (5) but implies a rather high activation energy of ~15 kcal $mole^{-1}$ for the diffusion process. A greater congestion of suitable adsorption sites on the young material is perhaps implied by the exp (-19.2θ) term, compared with exp (-11θ) in Eq. (6). An alternative, and perhaps more satisfactory explanation is to regard the $P^{1-\frac{1}{2}\theta}$ term [and the fractional powers of P in Eqs. (6) and (3)] as due to variations in the degree of reversibility of the adsorption at the temperatures at which the pressure dependence was measured; in any case the fact that desorption is proceeding at the same time as adsorption means that the true activation energy for the adsorption step at zero coverage is somewhat greater than that given in Eqs. (1), (3), and (6).

It is generally assumed that oxygen chemisorption must occur on exposed Ni^{2+} ions but that these will be withdrawn somewhat below the surface wherever possible. The experiments recorded above in the section "Stability of Adsorbents," in which it was found that keeping a freshly outgassed sample isolated *in vacuo* for many hours at ~100°C reduced markedly its capacity to adsorb oxygen, and also changed the distribution of the remaining active sites, are of interest in this connection. We can argue that outgassing at 500°C produces a certain number of exposed Ni^{2+} ions; on cooling these begin to relax into the lattice or migrate inwards down the boundaries between the magnetic domains; some will complete this process, but on fairly rapid cooling such as we employed it may be expected that the relaxation process will lag behind the temperature. Similar remarks apply if instead of exposed Ni^{2+} the adsorption requires the presence (or absence) of some special aggregation of defects or impurities. On passing through the Néel point the surface will be largely frozen in the configuration existing at the moment the magnetic domains are reformed, probably with all the exposed Ni^{2+} concentrated along the domain boundaries. Rapid cooling to the adsorption temperature and the commencement of adsorption within a short time will give, as we have found, reasonably reproducible results (although the surface will be that characteristic of some higher, unknown, temperature). Long annealing at the adsorption temperature will, however, allow a considerable relaxation of the surface (including perhaps the association of P^+ with adsorption sites, thus rendering them inactive) with a pronounced fall in reactivity, as found. In this connection we may note that Charman and Dell (*25*) record an abrupt increase in the rate of healing of fast neutron damage (as measured by the amount of irreversible fast O_2 adsorption at room temperature) in NiO when the specimens were annealed at 250°C for 2 hr compared with 2 hr at 200°C; we associate this with the relaxation which occurs on passing up and down through the Néel point.

We have commented elsewhere (*5*) that the large changes in surface area which our materials have suffered may well be due, at least in part, to the continual formation and destruction of the magnetic domains during thermal cycling through the Néel temperature. Further work has shown that ~60 cycles through the Néel point (i.e., from room temperature to 500°C and back) of a sample of NiO, thoroughly evacuated and sealed off *in vacuo*, caused the surface area to double; a control sample kept for the same period of time (6 weeks) at 500°C suffered no change in area. Some recrystallization will occur in time, relieving the lattice strain along the T twin boundaries. Thus Slack (*16*c) has pointed out that strain along the boundary between two domains separated by a T wall can be relieved by the formation of a fissure along the line of the wall with an angle of 12′ of arc. Such fissures emerging at or lying in the surface, provide a satisfactory explanation for the observed increases in area. The process of relaxation will be aided by oxygen exchange between adsorbed gases and the lattice which should facilitate geometric changes in the surface. Electron microscope examination by us has, however, so far not yielded convincing evidence of such fissures.

E. General

Our model of the adsorption process as an essentially localized event, not much affected by the general defect structure of the solid is in accord with the present view of the conduction process in NiO and the absence of a *d* band due to the localization of the 3*d* orbitals of the cations. It is in agreement with our earlier opinion (*19*) that the boundary layer theory of chemisorption is not directly applicable to many semiconductors, and accords with the recent work on NiO of Cotton and Fensham (*27*). It has been suggested that application of crystal field theory to particular surface models (*28*) may lead to useful correlations and this may well prove to be the case, particularly around room temperature. It has, however, recently been pointed out (*29*) that the energies involved are very small compared with the other terms involved such as the Magdelung and Coulomb energies. Certainly a recent claim to have measured crystal field effects by photodesorption of O_2 from NiO (*30*) has been challenged on both experimental and theoretical grounds (*31*). It appears that the observed effect was a thermal desorption of weakly bound molecular oxygen and we suggest that the species concerned is that which we have designated $O_{2(a)}$, which is the main form adsorbed around room temperature and below.

The chemisorption of oxygen as mainly O_2^- below 250°C and as 2 O^- above that temperature provides a plausible reason for the change in mechanism of the CO–O_2 oxidation catalyzed by NiO which is generally believed to occur at about this temperature (*26*). Thus the first product of the surface reaction below 250°C may be a CO_3^- complex which decomposes to CO_2 [possibly with cooperative interaction with another molecule of CO (*19*)] by a process requiring say 0–5 kcals mole^{-1}. Above 250°C the first product would be a CO_2^- complex, requiring considerably more energy for its decomposition into gaseous CO_2. Slow formation of CO_2^- can readily be formulated, either as a side reaction or upon unusually active sites below 250°, and explains the slow poisoning "by CO_2" found at the lower temperatures.

Finally we wish to emphasize that our arguments and conclusions will not apply in all details to other forms of NiO which have been widely studied. Thus the oxide of high surface area (100–200 m^{2}g^{-1}) prepared by slow decomposition *in vacuo* of the hydroxide may be too finely divided to form more than one magnetic domain per particle: This oxide is very active and adsorbs more O_2 than our NiO. The adsorption is accompanied by a marked darkening which is not observed with coarser powders. Undoubtedly this material has a very open structure [an area of 210 m^{2}g^{-1} means that something like one in four of the Ni^{2+} will be in the surface (*27*)] and this will certainly mean a different distribution of sites from that found in the coarser materials. This oxide differs significantly in its magnetic properties from coarser materials, the value of T_N depending on the particle size so that values below 200°K were found for very fine powders (*35*). Such low values lead us to predict, from our model of the adsorption process, that the adsorption of O_2 at room temperature upon the oxide of high surface area used by Teichner *et al.* will occur as O^-, and this indeed is the interpretation he has put upon his calorimetric data (*36*). Similarly films of NiO upon Ni may well have their structure and topography influenced by the grain of the underlying metal (*32*), which may also affect the magnetic domain structure. The presence of a concentration gradient of Ni atoms below the gas–oxide interface will here also tend to promote the formation of O^- rather than O_2^- at room temperature and to lead to less reversibility. Calorimetric measurements upon this material also have been interpreted in terms of the adsorption of O_2 as O^- at least in the initial stages of the adsorption (*33*). Our present results are also in sharp contrast to the earlier observations upon unaged NiO prepared from the carbonate where, at higher pressures we found the activation energy for O_2 adsorption rose from about zero at low coverage to about 35 kcal mole^{-1} at saturation in the temperature range 400° to 460°C (*34*).

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REFERENCES

1. (a) Charman, H. B., Dell, R. M., and Teale, S. S., *Trans. Faraday Soc.* **59,** 453 (1963); (b) Cotton, J. D., and Fensham, P. J., *Trans. Faraday Soc.* **59,** 1444 (1963).

2. Winter, E. R. S., *Discussions Faraday Soc.* **28,** 183 (1959).

3. Winter, E. R. S., *J. Chem. Soc.* (*London*), pp. 1509, 1522 (1954).

4. Winter, E. R. S., *J. Sci. Instr.* **38,** 345 (1961).

5. Eaton, L. D., and Winter, E. R. S., *J. Catalysis* **4,** 552 (1965).

6. Brownlee, L. D., and Mitchell, E. W. J., *Proc. Phys. Soc.* (*London*) **B65,** 710 (1952).

7. Parravano, G., *J. Chem. Phys.* **23,** 5 (1955).

8. Kutseva, L. N., and Keier, M. P., *Probl. Kinetiki i Kataliza, Akad. Nauk SSSR* **10,** 82 (1960); *ibid., Izv. Akad. Nauk, SSSR* **5,** 797 (1959).

9. Deren, J., Haber, J., and Skoczynski, J., *Trans. Faraday Soc.* **58,** 166 (1962).

10. Winter, E. R. S., unpublished.

11. Popovskii, V., and Boreskov, G. K., *Kinetika i Kataliz* **1,** 566, (1960); Boreskov, G. K., and Popovskii, V., *Kinetika i Kataliz* **2,** 657 (1961); Dzizyak, A. P., Boreskov, G. K., and Kasatkina, K. A., *Kinetika i Kataliz* **3,** 81 (1962).

12. (a) Foex, M., *Compt. Rend.* **227,** 193 (1948); (b) Heikes, R. R., and Johnston, W. D., *J. Chem. Phys.* **26,** 582 (1957).

13. Perakis, N., Wucher, J., and Parravano, G., *Compt. Rend.* **248,** 2306 (1959).

14. Cimino, A., Molinari, E., and Romeo, G., *Z. Physik. Chem.* (*Leipzig*) **16,** 101 (1958); Parravano, G., and Boudart, M., *Advan. Catalysis* **7,** 66 (1955); Bielanski, A., and Haber, J., *Z. Physik. Chem.* (*Leipzig*) **24,** 345 (1960); Mehandjiev, D., and Bliznakov, G., *Proc. Intern. Congr. Catalysis, 3rd, Amsterdam, 1964,* 781 (1965).

15. Engell, H. J., and Hauffe, K., *Z. Elecktrochem.* **57,** 762, 773 (1953).

16. (a) Roth, W. L., *Phys. Rev.* **111,** 772 (1958); (b) *ibid., J. Appl. Phys.* **31,** 2000 (1960); (c) Slack, G. A., *J. Appl. Phys.* **31,** 1571 (1960).

17. Street, R., and Lewis, B., *Nature* **168,** 1036 (1951).

18. Van Houten, S., *J. Phys. Chem. Solids* **17,** 7 (1960).

19. Winter, E. R. S., *Advan. Catalysis* **10,** 196 (1958).

20. Gossel, H., *Z. Elecktrochem.* **65,** 98 (1961).

21. Bielanski, A., Deren, J., Haber, J., and Slocynski, J., *Trans. Faraday Soc.* **58,** 166 (1962).

22. Morin, F. T., *Phys. Rev.* **93,** 1199 (1954).

23. Miller, A. R., "Adsorption of Gases on Solids," p. 57. Cambridge University Press, Cambridge, England, 1949.

24. Winter, E. R. S., *J. Catalysis* **4,** 134 (1965).

25. Charman, H. B., and Dell, R. M., *Trans. Faraday Soc.* **59,** 470 (1963).

26. Dry, M. E., and Stone, F. S., *Discussions Faraday Soc.* **28,** 192 (1959); Winter, E. R. S., *ibid.*, p. 216.

27. Cotton, J. D., and Fensham, P. J., *Trans. Faraday Soc.* **59,** 1444 (1963).

28. Dowden, D. A., and Wells, D., *Actes Congr. Intern. Catalyse, 2^e, Paris, 1960,* p. 1499 (1961).

29. Dickens, P. G., and Sutcliffe, M. B., *Trans. Faraday Soc.* **60,** 1272 (1964); Goodenough, J. B., "Magnetism and the Chemical Bond," p. 163. Wiley, New York, 1963.

30. Haber, J., and Stone, F. S., *Trans. Faraday Soc.* **59,** 192 (1963).

31. Jongepier, R., and Schuit, G. C. A., *J. Catalysis* **3,** 464 (1964); Kotel'nikov, V. A., *Kinetika i Kataliz* **5,** 565 (1964).

32. Martius, U., *Discussions Faraday Soc.* **28,** 220 (1959).

33. Stone, F. S., *Advan. Catalysis* **13,** 1 (1962).

34. Winter, E. R. S., *J. Chem. Soc.* (*London*), p. 3824 (1955).

35. Richardson, J. T., and Milligan, W. O., *Phys. Rev.* **102,** 1289 (1956).

36. Coue, J., Gravelle, P. C., Ranc, R. E., Rue, P., and Teichner, S. J., *Proc. Intern. Congr. Catalysis, 3rd, Amsterdam, 1964,* p. 748 (1965).