

The Decomposition of Nitrous Oxide on Metallic Oxides

Part II*

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The preexponential term and the activation energy in the Arrhenius expression for the decomposition of N_2O on many oxide catalysts and the rate of the reaction at a given temperature show fairly strong correlations with the corresponding functions for the isotopic exchange between O_2 gas and the oxide surface. There thus exists a correlation between the activation energy of the decomposition reaction and lattice parameter of the catalyst, but this is weaker than that found for the rare-earth series. The correlation between lattice parameter and the preexponential term is almost completely obscured, presumably by specific chemical interactions which are not detectable in the rare-earth series, but there is nevertheless a correlation between lattice parameter and the rate of reaction at a given temperature for each crystal structure.

INTRODUCTION

The strong correlations between the Arrhenius parameters for the N_2O -decomposition reaction and the isotopic exchange between gaseous oxygen and the oxide surface found for the rare-earth oxides (1) are perhaps not unexpected in view of the close chemical similarity which exists in this series. Even here, however, the correspondence was not perfect and it was clearly desirable to test the relationship over a wide range of metallic oxides.

METHOD

(a) **Materials.** The oxides were the samples used in the earlier (2) work upon ^{18}O exchange: N_2O and O_2 were prepared as before (1).

(b) **Kinetic and adsorption measurements.** These were performed as before (1).

KINETICS

The kinetic analysis and discussion of Part I (1) applies also to the present work:

* Part I, The decomposition of nitrous oxide on the rare-earth sesquioxides and related oxides. *J. Catal.* 15, 144 (1969) (1).

the symbolism used in that paper will be used here.

RESULTS

BET areas of the catalysts are given elsewhere (2). The kinetic measurements at initial N_2O pressures of between 10 and 20 cm are summarized in Table 1 and the adsorption measurements in Table 2. The kinetics were generally adequately described by Eq. (9) of Part I:

$$-\frac{d[P_{N_2O}]}{dt} = K \frac{[P_{N_2O}]}{[P_{O_2}]^{1/2}}, \quad (1)$$

but it is again to be noted that a detailed examination of the kinetics has not been attempted, and a few experiments showed some curvature in what should have been a linear plot of the integrated form of the above equation (i.e., Eq. (10) of Part I).

DISCUSSION

We have shown (1) that the rate constant of Eq. (1) is given with reasonable accuracy by

$$K = \frac{kK_1N}{[K_3]^{1/2}} \quad (2)$$

TABLE I
 KINETIC RESULTS

Oxide	T(°C) ^a	E ₁ ^b	Log ₁₀ (A ₁) ^c	Log ₁₀ (K) ^c	E _B ^b	$\frac{1}{2}$ Log ₁₀ (A _B) ^d	$\frac{1}{2}$ Log ₁₀ (B) ^d
BeO	550-660	37	2.02	-9.09	44.5	10.17	3.49
MgO	450-550	35	2.57	-7.94	38	11.34	5.64
NiO	400-500	39.5	5.36	-6.50	45	13.25	6.49
ZnO	530-610	41	3.83	-8.49	36	10.50	5.09
CaO	170-380	34	4.74	-5.47	30	10.79	6.29
SrO	420-540	23	0.94	-5.97	15	8.37	6.11
Al ₂ O ₃	530-660	43	3.43	-9.47	45	11.02	4.26
Fe ₂ O ₃	280-460	22	0.41	-6.20	27	10.24	6.19
Cr ₂ O ₃	450-570	40	3.81	-8.20	34	11.31	6.20
Ga ₂ O ₃	540-640	40.5	3.12	-9.05	40.5	10.93	5.35
CeO ₂	400-500	26	0.43	-7.38	26	9.64	5.73
HfO ₂	480-540	30	2.96	-6.06	30	9.84	5.33
ThO ₂	420-500	30	2.24	-6.77	22	9.22	5.91
SnO ₂	430-550	32	2.39	-7.22	27	9.40	5.35
TiO ₂	540-680	39	2.03	-9.68	35	10.22	4.91
CuO	340-410	24	1.63	-5.58	22	11.72	8.41
Rh ₂ O ₃	280-380	34	6.97	-3.28	10	7.61	6.11
MnO ₂	410-480	30	2.18	-6.83	15	8.17	5.91
IrO ₂	250-350	30.5	5.09	-4.07	24	12.30	8.69

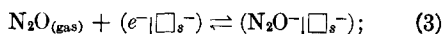
^a Reaction temperature range.

^b kcal mole⁻¹.

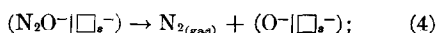
^c *K* and *A*₁ in [dynes cm⁻²]^{1/2} sec⁻¹ cm⁻² of catalyst surface in a reaction volume of 320 ml; *K* is the rate at 450°C.

^d *B* and *A*_B in molecules sec⁻¹ cm⁻² of catalyst surface; *E*_B, *A*_B, and *B* taken from Ref. (2).

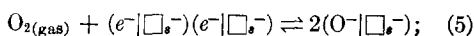
where *K*₁ is the equilibrium constant for the chemisorption of N₂O



and *k* is the rate constant for the decomposition of chemisorbed N₂O



*K*₃ is the equilibrium constant for the chemisorption of O₂:



and *N* is the total number of active surface sites.

*K*₃ may be expressed as

$$K_3 = \frac{\alpha}{\mu B}, \quad (6)$$

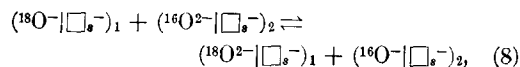
where (α/μ) is roughly constant; $\mu = (2\pi mkT)^{1/2}$; α is the accommodation coefficient for O₂ molecules; and *B* is the rate of desorption of O₂ molecules.

We write *K* and *B* in the Arrhenius form:

$$K = A_1 \exp(-E_1/RT);$$

$$B = A_B \exp(-E_B/RT) \quad (7)$$

We have shown (1, 2) that, for oxides where isotopic exchange between gaseous oxygen and the oxide surface occurs by the atomic mechanism [i.e., Eq. (5) above written with ¹⁸O, followed by a charge-exchange



where the subscripts identify surface sites] we may equate *B* to the observed rate constant for the exchange reaction: values of *B*, *A*_B, and *E*_B for the oxides examined here have been reported elsewhere (2). It then follows for such oxides that the following relationships may hold between the parameters of the oxygen exchange and of the nitrous oxide decomposition reaction:

$$E_1 \propto E_B, \quad (9)$$

and

$$\log_{10} [A_1] \propto \log_{10} [A_B].$$

TABLE 2
 SUMMARY OF ADSORPTION MEASUREMENTS FOR N₂O

Oxide	T(°C) ^a	Adsorption of N ₂ O molecules (cm ⁻²)			
		At 3.4 mm ^b	At 0.18 mm ^c	E _H ^d	-E _L ^e
BeO	335-435	6.2 × 10 ¹¹	8.4 × 10 ¹⁰	10	15
MgO	200-300	— ^f	3.0 × 10 ⁹	—	0
NiO	160-250	3.6 × 10 ¹²	5.1 × 10 ¹¹	4	
ZnO	175-310	3.5 × 10 ^{12g}	5.1 × 10 ¹¹	7.5	10.5
CaO ^h	90-190	1.5 × 10 ¹²	1.6 × 10 ¹¹	3.5	6.5
SrO	100-240	2.8 × 10 ¹²	1.7 × 10 ¹²	5.5	3.5
Al ₂ O ₃	350-445	1.3 × 10 ¹¹	4.9 × 10 ⁹	—	—
Fe ₂ O ₃	200-290	6.7 × 10 ¹¹	5.2 × 10 ¹⁰	5	2
Cr ₂ O ₃	260-350	4.4 × 10 ¹¹	4.3 × 10 ¹⁰	0	0
Ga ₂ O ₃	130-230	9.2 × 10 ¹¹	9.7 × 10 ¹⁰	3	6
CeO ₂	100-300	2.2 × 10 ¹²	9.8 × 10 ¹¹	6	6
HfO ₂	80-180	1.4 × 10 ¹²	1.9 × 10 ¹²	9	11
ThO ₂	290-370	1.8 × 10 ¹²	1.6 × 10 ¹¹	4	5
SnO ₂	145-325	5.2 × 10 ¹¹	8.7 × 10 ¹⁰	5.5	5.5
TiO ₂	80-325	6.2 × 10 ¹¹	1.6 × 10 ¹¹	2	2
CuO	110-200	4.4 × 10 ¹¹	1.2 × 10 ¹¹	4	5
Rh ₂ O ₃	210-280	4.9 × 10 ¹²	4.2 × 10 ¹¹	9	20
MnO ₂	210-260	1.5 × 10 ¹²	3.2 × 10 ¹⁰	0	5
IrO ₂	130-210	5.7 × 10 ¹²	6.8 × 10 ¹¹	2.5	5

^a Temperature range of observations.

^b At the highest temperature; and ^c at the lowest temperature of column 2; adsorption was also measured at one intermediate pressure.

^d Apparent activation energy (kcal) from the *decrease* with increasing temperature of the quantity adsorbed at 3.4 mm: estimated uncertainty ±2 kcal. ^e Same for 0.18 mm.

^f Too small to measure.

^g At 200°C.

^h A fresh preparation: not that used for the kinetic measurements.

The first 15 oxides of Table 1 exchange with oxygen substantially by Eqs. (5) and (8) and we consider these in detail now: Table 1 contains, for easy reference, the oxygen-exchange results reported in detail elsewhere (2).

Figures 1 and 2 show the relationships of Eq. (9): it was shown in Part I that the slopes of the straight lines should be 1 and 0.5, respectively. The line drawn in Fig. 1 is the regression of $\frac{1}{2}E_B$ (or y) upon E_1 (or x) and its equation is

$$y = 0.793x - 10.57, \quad (10)$$

with a correlation coefficient of 0.83 which is significant at better than the 0.001 level for 15 pairs of observations (3). Similarly the line drawn in Fig. 2 is the regression of $\frac{1}{2} \log(A_B)$ (or y) upon $\log(A_1)$ (or x) and its equation is

$$y = 0.569x + 8.89, \quad (11)$$

with a correlation coefficient of 0.70 which is significant at between the 0.01 and 0.001 levels.

In view of this correspondence between the parameters in the two rate expressions we would expect a similar correspondence between the rates of the two reactions at temperatures covered by the range of experiments: Figure 3 shows such a correspondence at 450°C. The line drawn is the regression of y upon x and has the equation

$$y = -0.76x + 11.25, \quad (12)$$

where $y = \frac{1}{2} \log(B)$ and $x = -\log(K)$ with a correlation coefficient of 0.81: the significance is of the same order at 400 and 500°C.

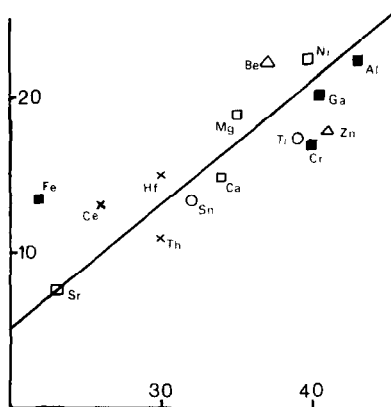


FIG. 1. Variation of the activation energy for N₂O decomposition with that for the oxygen-exchange reaction: abscissa, E_1 ; ordinate, $\frac{1}{2} E_B$, both in kcal mole⁻¹.

The previous paragraph indicates a fairly uniform kinetic picture throughout this set of oxides and therefore it is not unexpected that the compensation effect for the N₂O-decomposition reaction has a similar level of significance. Figure 4 shows a plot of E_1 against $\log(A_1)$; the line drawn is the regression of E_1 (y) upon $\log(A_1)$ (x):

$$y = 3.40x + 25.01, \quad (13)$$

with a correlation coefficient of 0.73 for the 15 catalysts.

It was shown in Part I that the correlations found in Figs. 1-3 and Eqs. (10)-(12)

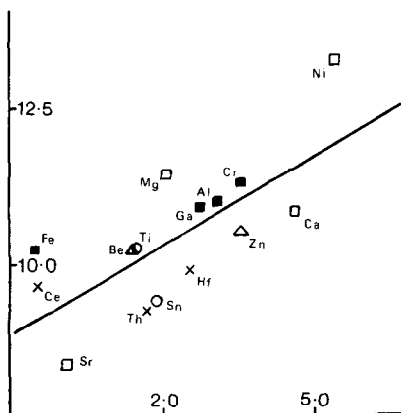


FIG. 2. Relationship between the preexponential terms of the rate expressions for the N₂O decomposition and oxygen-exchange reaction: abscissa, $\log_{10}(A_1)$; ordinate, $\frac{1}{2} \log_{10}(A_B)$ (see Table 1 for units).

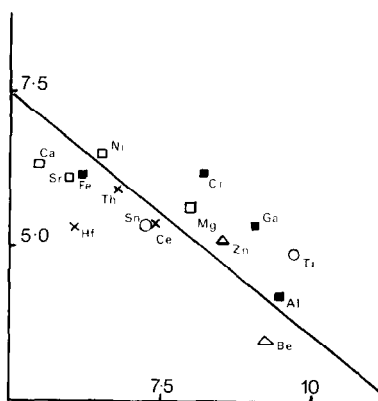


FIG. 3. Dependence at 450°C of the rate of N₂O decomposition upon the rate of oxygen exchange: abscissa, $\log_{10}(K)$; ordinate, $\frac{1}{2} \log_{10}(B)$ (see Table 1 for units).

over a series of catalysts imply that the most important reaction determining changes in the rate (and E) of the N₂O decomposition across the series of oxides is the desorption of O₂, that is that the variation across the series of the rate (and free energy change) of chemisorption of N₂O and its subsequent decomposition to gaseous nitrogen and O_(ads) [reactions (3) and (4) above] are much less important in determining changes in the overall rate. It is important to note that these results do not mean that the desorption of oxygen is rate determining: the derivation (1, 4) of Eqs. (1) and (2) shows clearly that the slow step is the decomposition of the adsorbed N₂O by Eq. (4): Stone (5) wrongly

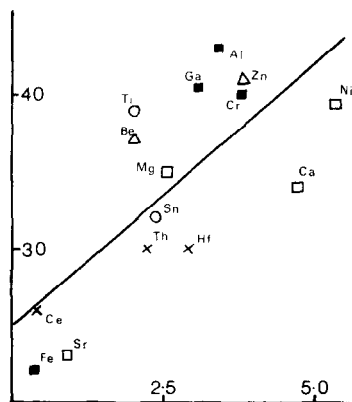


FIG. 4. The compensation effect for the N₂O decomposition: abscissa, $\log_{10}(A_1)$ (Table 1); ordinate, E_1 .

attributes to us (4) the conclusion that the formation of this adsorption complex is the slow step. The overall rate is determined in part by the number of reaction sites available for N_2O chemisorption, which number is determined by the competition between the two equilibria of Eqs. (3) and (5) that is the oxygen acts as a poison to the N_2O decomposition. There is thus a clear difference between our findings and the conclusions of Hauffe *et al.* (6) based upon semiconductivity and boundary theory arguments and on cruder, less accurate kinetic studies (7) that the desorption of oxygen is, in general, the slow step although he was correct in concluding that changes in the rate and activation energy of desorption of O_2 largely control the corresponding changes in the kinetics of the N_2O decomposition from one catalyst to another.

It is not practicable to investigate reactions (3) and (4) at the temperatures and pressures used for the kinetic studies of Table 1. Table 2 however shows that at rather lower temperatures and pressures the adsorption does not vary much with temperature, except for ZnO , HfO_2 , BeO , and Rh_2O_3 so that with these exceptions the effect upon E_1 should be small. It was evident from the shape of the uptake vs. time curves that, as expected, in all cases where the adsorption was measurable, the process is an activated one as was first shown by us (9) for NiO and Cr_2O_3 , the activation energy being small in agreement with the low value (ca. 0.2 eV) for the threshold energy for electron capture by N_2O in the gas phase (8). The amount of adsorption (molecules per unit area) does not vary widely from one oxide to another and in all cases where measurement was possible the amount of adsorption was pressure-dependent and showed no signs of approaching saturation over the pressure range studied. These adsorption measurements were performed, as in Part I, by admitting small doses of N_2O to the freshly-outgassed oxides, measuring the pressure change in a fixed volume at frequent intervals, and extrapolating back to zero time. It was necessary to work at lower temperatures than those used in the

kinetic experiments, otherwise the decomposition masked the adsorption. Comparison of the second columns of Tables 1 and 2 shows that the reduction in temperature necessary varied widely. If we define the reduction ΔT as the difference between the lowest temperature in Table 1 column 2 and the highest in the corresponding column of Table 2 for each oxide, then ΔT varies from 0 for Fe_2O_3 and Rh_2O_3 to 300° for CeO_2 : there is no evidence of any systematic variation with oxide type or lattice parameter. Thus although the amount of adsorption per square centimeter recorded at 3.4 mm in the third column does not show much variation, consideration of the values of ΔT and of E_H , together with the probable variation with increasing pressure, indicates that the pre-exponential term A_1 may be seriously affected across the series of oxides. The kinetic analysis also assumes that the total number N of catalytic sites does not vary with temperature.

These factors and variation in k [Eq. (4)] are the main cause of the scatter in the figures and for the differences between the expected and the observed slopes of the regression lines.

There is little direct evidence upon the variation of the activation energy for reaction (4) from one catalyst to another: in the rare-earth series the reaction at low pressures was sufficiently reproducible to enable it to be established (1) that

$$E_1 \sim E_e + \frac{1}{2}E_B, \quad (14)$$

where E_e is the apparent activation energy of the decomposition at ca. 2 mm N_2O pressure and describes the temperature variation of the product (kK_1N). Earlier work at low pressures has indicated that generally the overall activation energy is distinctly less than at high pressures (10). In the present series, the measurements at low pressure were too irreproducible to merit serious consideration although it was established that, as for the rare-earth oxides $E_1 > E_e$; the initial velocity at ca. 2 mm was in general less than $1/10$ that at 10 cm. The irreproducibility was clearly associated with the difficulty of establishing standard surface reactivity for each run:

no procedure was found which was satisfactory in this respect for all the oxides, nor even was any method found which was satisfactory for all oxides of one type (e.g., *n*- or *p*-conductors).

The results and correlation discussed above provide a more satisfactory explanation of the variation in catalytic activity for the N₂O decomposition from one oxide to another than the earlier arguments based upon semiconductor properties and boundary layer theory. Instead of a crude division into good catalysts (*p*-type) and bad ones (*n*-type) with insulators mainly occupying an intermediate position (6, 11) the catalytic activity is controlled mainly by oxide type and lattice parameter, in a similar manner to the oxygen exchange reaction, due to the importance of the desorption of oxygen step. The earlier classification was very approximate except for extremes of reactivity, as it was based upon, in the main, scanty kinetic data and ignored possible changes in catalyst area from oxide to oxide (7).

We show in Fig. 5 a plot of the apparent activation energy, E_1 , for the N₂O decomposition at 10–20 cm against oxide lattice parameter in the form of [molecular vol]^{1/3}. The plot is very similar to the corresponding plot for the oxygen exchange reaction [Fig. 2 of Ref. (2)] and clearly divides the oxides into 3 types—the rock-salt MO oxides, the corundum M₂O₃ series, and the MO₂, both rutile and fluorite types lying around the same line. As with the exchange reaction the position of the two

wurtzite-type oxides BeO and ZnO is uncertain. The fall of E_1 with increasing lattice parameter is evident for each series but as expected due to the greater complexity of the N₂O reaction, discussed above, is not so regular as in the case of the exchange reaction. A plot of E_1 versus the nearest 0–0 distance is shown in Fig. 6 and is very similar to Fig. 5 of Ref. (2).

Line A in Fig. 6 is the regression line of E_1 (y) upon nearest 0–0 distance for the 15 rare-earth oxides considered in Part I (1); its equation is

$$y = -48.8x + 1.62,$$

with a correlation coefficient of 0.61 which is significant at between the 0.01 and 0.02 levels. Line B is the corresponding line for the rare-earth oxides and 8 other oxides examined in the present paper: the points for these 8 are plotted in Fig. 6 but the rare-earths are, for clarity, omitted. The equation of line B is

$$y = -37.9x + 1.33,$$

with a correlation coefficient for 23 pairs of observations of 0.48 which is significant at about the 0.02 level.

The MO oxides, also shown in Fig. 6, fall around another line, as noted for the oxygen exchange reaction (1): here also the position of BeO and ZnO is uncertain and ZnO at least appears not to fall in with the remaining M–O oxides. Of the remainder only Fe₂O₃ appears badly discordant: here, as is discussed below, there

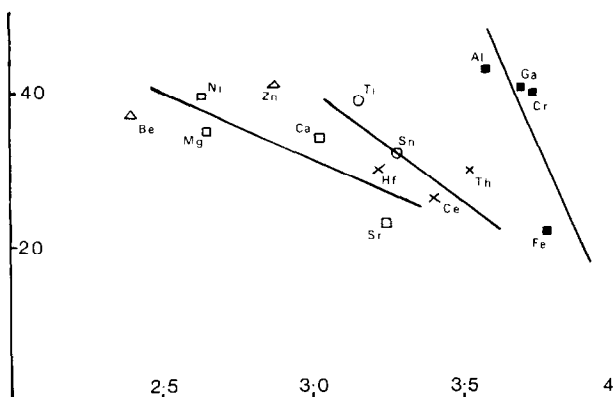


FIG. 5. Variation of the activation energy with lattice parameter and crystal type for the N₂O decomposition: abscissa, [molecular vol]^{1/3} Å³ molecule⁻¹; ordinate, E_1 kcal mole⁻¹.

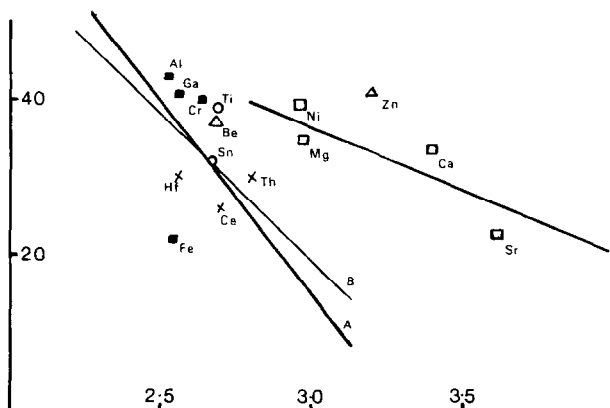


FIG. 6. Dependence of the activation energy for the N_2O decomposition upon nearest O-O distance: abscissa, nearest O-O distance Å; ordinate, E_1 kcal mole $^{-1}$.

is possible interference by another mechanism of oxygen exchange.

In the case of the exchange reaction, similar plots to Fig. 5 and 6 were found using $\log(A)$ instead of E , because of the strong compensation effect which existed between these two parameters for this reaction. However, although the compensation effect exists for the N_2O reaction, it is of less significance, and the scatter in Fig. 4 is considerable: in consequence a plot of $\log(A_1)$ against lattice parameters shows no regularity (Fig. 7). This blurring of systematic correlations as the complexity of the reaction increases is of interest, but of course is to be expected; as is evident from the discussion above, and from Eqs. (2) and (6) it is due to the inclusion of the terms $k K_1 N(\mu/\alpha)^{1/2}$ in the rate expres-

sion. In spite of the lack of correlation in Fig. 7, it is nevertheless found that the rate of reaction at a given temperature still varies in a systematic manner with lattice parameter. Figure 8 shows this for a temperature of $450^\circ C$: in this plot only the rate on HfO_2 seems seriously different from the expected value.

Although, in this discussion of our observations, we are placing the main emphasis upon the dependence of the reaction parameters upon crystal type and lattice spacing it is of course quite likely that some of the deviations from this simple relationship are due to causes which can be linked to the semiconductor type. The most likely step to be so influenced is the chemisorption of N_2O which might be written:

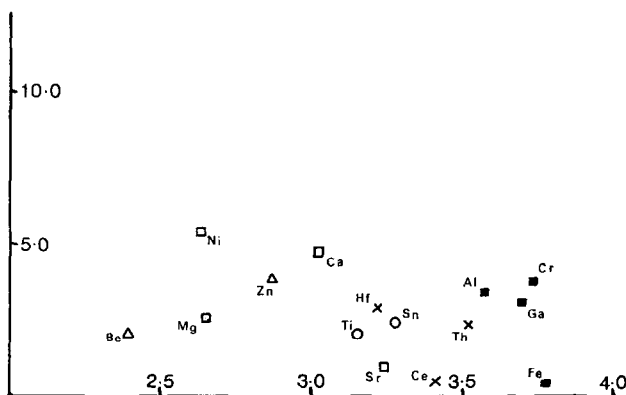


FIG. 7. The preexponential term for the N_2O decomposition plotted against lattice parameter: abscissa, molecular vol] $^{1/3}$ Å molecule $^{-1}$; ordinate, $\log_{10}(A_1)$.

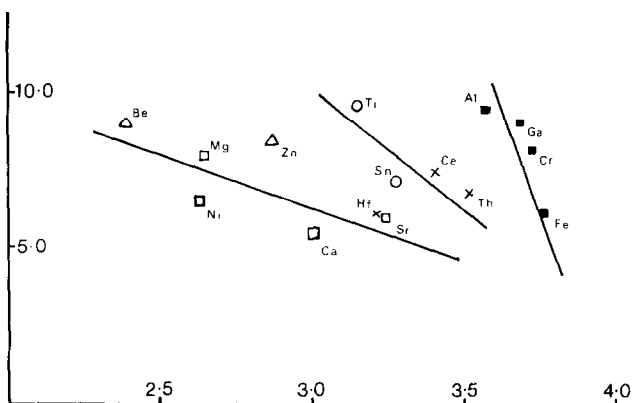
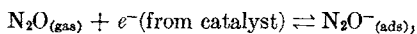


FIG. 8. Dependence at 450°C of the rate of N₂O decomposition upon lattice parameter and crystal type: abscissa, [molecular vol]^{1/2}; Å molecule⁻¹; ordinate, log₁₀ (*K*) at 450°C, Table 1.



but no clear generalization along these lines emerges from an examination of Tables 1 and 2 and the accompanying figures.

Results for the oxides CuO, MnO₂, Rh₂O₃, and IrO₂ are also given in Tables 1 and 2: these have been excluded from the figures and from the discussion above because the oxygen-exchange reaction for these oxides proceeds to a large extent or entirely by the molecular mechanism (2). This envisages that exchange occurs by the chemisorption of a molecule of oxygen and the simultaneous desorption of a molecule from a pair of adjacent sites: dissociation into O⁻_(ads) and subsequent charge-exchange [reactions (5) and (8)] are assumed to be much less important in the exchange reaction (or nonexistent) on these oxides. (It may be remarked that Fe₂O₃, NiO, and Cr₂O₃ also exhibit appreciable molecular exchange but in these cases reasonably accurate values for the dissociative exchange parameters were obtained. The presence, simultaneously, of the two reactions could account for some of the scatter in the above figures.) If these four oxides are inserted in Figs. 1-4 and the extent of their deviation from the regression lines of Eqs. (10)-(13) is examined, it is found that:

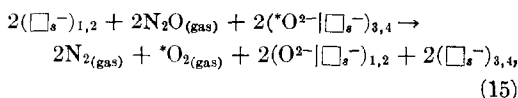
Figure 1. Rh and Mn are in poor agreement (but no worse than Fe): Ir and Cu are in good agreement.

Figure 2. Only Cu is in poor agreement (but so is Fe).

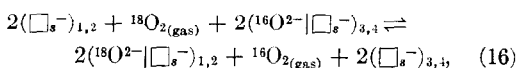
Figure 3. Only Rh is in poor agreement.

Figure 4. These four oxides appear to follow a straightline relationship of different (lower) slope from the remaining 15: this behavior is similar to that observed in the oxygen exchange reaction.

These observations indicate that for these oxides also there is a reasonably close correlation between the two reactions. It might be expected that on these catalysts the reaction would be of the second order in N₂O because the reaction might be:



where the asterisk identifies catalyst surface oxygen, by analogy with the exchange reaction:



where the subscripts identify the surface sites concerned. However, in the range 5-30 cm initial pressure of N₂O, the kinetic observations for these oxides fitted the general expression (4):

$$-\frac{d[\text{N}_2\text{O}]}{dt} = \frac{k[\text{N}_2\text{O}]}{1 + a[\text{N}_2\text{O}] + b[\text{O}_2]^n} \quad (17)$$

(where *a*, *b*, and *k* are constants and the brackets represent gas pressures and *n* = 1 or 1/2) or the simplified form of Eq. (1) as well as any expression involving

$[\text{N}_2\text{O}]^2$ and $[\text{O}_2]$. In view of the 3 disposable parameters in Eq. (17) this is not surprising. There is thus no evidence for a change of mechanism: nevertheless the general agreement of these oxides with the patterns established for the other 15 is unexpected. Table 1 shows that these four oxides are more reactive than the majority of the remainder: CuO and IrO_2 are particularly active: the high activity of CuO has been noticed in earlier work (6).

Unlike the earlier correlation (6, 11), the present paper associates changes in catalytic activity with changes in the characteristics of the oxygen desorption reaction. This latter reaction, in the case of all the oxides considered here except probably CuO, Rh_2O_3 , MnO_2 and IrO_2 , is closely related to the crystal structure and changes in the lattice parameter and, as discussed in detail elsewhere (2), not directly to the semiconductivity type of the oxide. This observation indicates that the electronic factor is much less important in controlling catalytic activity, at least in the present case, than has been believed. It is to be noted that, as we pointed out when discussing the oxygen-exchange reaction (2), the reaction parameters vary in similar manner with any chemical or physical property which changes regularly with lattice parameter. We have chosen, for reasons discussed in detail elsewhere (2), to relate the reaction parameters to lattice spacing and in particular to the minimum O-O distance; it is of course possible that other properties may after further investigation prove to be more significant.

The temperature range over which the N_2O reaction has been studied is given for each oxide in Table 1; comparison with the corresponding figures in Table 3 of Ref. (2) shows that in all cases the two reactions overlap, the N_2O reaction generally requiring a slightly higher temperature. In Part I the mechanism of the reaction was discussed in detail and it was shown that this means that in all probability the whole of the oxide surface takes part in the N_2O reaction, there being no localized (immobile) areas of high catalytic activity, i.e., the concept of "active centers" should

not be applied to the reaction at these temperatures. However, if the relationship of Fig. 6 is significant, and if we are correct in our analysis of the mechanism of the oxygen-exchange reaction (2) the desorption of the O_2 molecule may occur only from pairs of anion sites at the minimum O-O distance. In most cases the reactions have required the use of relatively high temperatures—both absolutely and in terms of the Tammann point for each oxide—for their study. It is unlikely that, at such temperatures, crystal field effects will be of much importance in determining the course or energetics of the reaction, since appreciable surface mobility must be present under reaction conditions. Such mobility must involve the compensation, or neutralization, of lattice forces much greater in magnitude than the crystal field stabilization forces.

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