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Catalysis of Isotope Exchange in Molecular Oxygen and Its Application to the Study of Catalysts

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Problems related to the kinetics and mechanism of isotope exchange in molecular oxygen on solid catalysts are reviewed. Experimental data on the homomolecular exchange of oxygen on oxides and metals are reported. The relationship between the catalytic activity of oxides towards oxygen exchange and their activity towards other oxidation reactions is discussed. It is pointed out that studies of isotope exchange reactions of molecular oxygen should prove useful in elucidating the nature of intermediate entities during the interaction of oxygen with a catalyst surface. The activity towards exchange can be used as a characteristic of general oxygen reactivity, and rules for the choice of oxidation catalysts can be based on it.

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I. INTRODUCTION

The exchange of atoms between oxygen molecules (homomolecular isotope exchange)

$$^{16}O_2 + {}^{18}O_2 = 2{}^{16}O{}^{18}O \qquad (1)$$

is the simplest chemical reaction which oxygen can undergo. This provides a very convenient model reaction for investigating the rules which control the choice of catalysts, since it is not accompanied by changes in the chemical composition of the reaction mixture. The features of the homomolecular isotope exchange reactions provide information on the nature of the oxygen bond on the catalyst surface and can be useful in explaining the mechanism of catalytic oxidation reactions. The analogous isotope exchange reaction in molecular hydrogen has been the object of a large number of investigations, and has played an important role in elucidating the mechanism of catalytic hydrogenation reactions.

Studies of homomolecular exchange in oxygen began relatively recently. The first results for this reaction on magnesium and zinc oxides[1] were published by Winter as recently as 1954; this paper was followed by a paper relating to some other oxides[2]. The early results were reviewed by Winter[3], and compared with data on the rate of isotope exchange between molecular oxygen and the oxygen from the oxides, the rate of adsorption and the catalytic activity towards the oxidation of CO and the decomposition of N_2O. In later years, a great deal of work on homomolecular exchange in oxygen was published by Soviet scientists[4-32]. Foreign workers also are active in this field[33-37].

The present review attempts to generalise the results obtained so far and to consider the various possible relationships between the activity of catalysts towards homomolecular oxygen exchange and their activity towards other oxidation reactions, involving the transfer of oxygen atoms between reactant molecules.

II. KINETICS OF ISOTOPE EXCHANGE IN MOLECULAR OXYGEN

1. Method of Investigation

The course of reaction (1) is monitored mass-spectrometrically from the change in the intensity ratio of the peaks corresponding to masses 32 ($^{16}O_2$), 34 ($^{16}O^{18}O$), and 36 ($^{18}O_2$). Winter[3] worked with a static system, taking a continuous leak of a very small fraction of the reaction mixture to the mass spectrometer tube through a fine capillary. Some workers have sampled the gas for isotopic analysis at intervals, by means of ampoules removed from the apparatus and transferred to the mass spectrometer. To avoid the possibility of diffusion-controlled steps at high rates of exchange it is desirable to work with a circulating system[6].

Isotope exchange in molecular oxygen has been studied mainly on oxides[1-4,6-10,33,34], and less extensively on metals[4,5,11,20-22,35,36]. With oxides, exchange between molecular oxygen and oxygen from the oxide is possible as well as homomolecular exchange. In most of the work on the isotope exchange of molecular oxygen on oxides, conditions were such that the concentrations of ^{18}O in the solid (α_s) and in the gas (α) were equal. Some workers[9,19,28,34] studied exchange in molecular oxygen under conditions of simultaneous isotope exchange between the oxygen in the oxide and in the gas phase.

2. Kinetics of Isotope Exchange in Molecular Oxygen in the Absence of Isotope Exchange with the Catalyst

The kinetics of homomolecular oxygen exchange are described in this case ($\alpha_s = \alpha$) by a first-order equation. For

example, the change in the concentration of $^{16}O^{18}O$ molecules is

$$\frac{dC_{34}}{d\tau} = Z\frac{S}{N_g}(C^*_{34} - C_{34}) = k(C^*_{34} - C_{34}) \quad (2)$$

where Z is the total number of oxygen molecules, whatever their isotopic composition, which exchange atoms per unit time and unit catalyst surface, in molecules cm^{-2} s^{-1}; N_g is the total number of oxygen molecules in the gas phase; S is the surface area of the catalyst in cm^2; τ is time in s; C^*_{34} and C_{34} are the fractional numbers of $^{16}O^{18}O$ molecules at equilibrium and at time τ respectively. Integration of Eqn. (2) gives

$$k = \frac{1}{\tau}\ln\frac{C^*_{34} - C^0_{34}}{C^*_{34} - C_{34}} \quad (2a)$$

where C^0_{34} is the fraction of $^{16}O^{18}O$ molecules at zero time.

Eqn. (2) is valid for any exchange mechanism[38]. The influence of the mechanism is manifest only in the dependence of the total number Z of exchanges upon the oxygen pressure P_{O_2} and the temperature T.

3. Kinetics of Exchange in Molecular Oxygen with Simultaneous Isotope Exchange with the Oxygen of the Catalyst

To elucidate the details of the exchange mechanism, it is often helpful to measure simultaneously the rates of exchange in molecular oxygen and of isotope exchange with the oxygen of the catalyst. In this case $\alpha \neq \alpha_s$, and the kinetics of the exchange become more complex.

Isotope exchange with the oxygen of the catalyst (for example, an oxide) includes dissociative adsorption with formation of adsorbed atoms or atomic ions, exchange of these adsorbed species with oxygen ions from the oxide, and desorption in the form of molecules[7].

The change in concentration of ^{18}O in the gas phase due to exchange with the oxygen of the catalyst is described by the equation

$$-\frac{d\alpha}{d\tau} = R\frac{S}{N_g}(\alpha - \alpha_s) = R'(\alpha - \alpha_s) \quad (3)$$

or, in the integral form,

$$R' = \frac{N_s}{N_g + N_s}\frac{1}{\tau}\ln\frac{\alpha^0 - \alpha^*}{\alpha - \alpha^*} \quad (3a)$$

Here R is the total number of exchanges between oxygen from the oxide and oxygen in the gas phase, in molecules cm^{-2} s^{-1}; N_s is the amount of accessible oxygen in the oxide (number of molecules); α^0, α^*, and α are the fractional amounts of ^{18}O at zero time, at equilibrium, and at time τ respectively.

The kinetics of exchange in molecular oxygen occurring simultaneously with isotope exchange with the oxygen of the catalyst have been considered in detail by Musykantov and coworkers[18]. Three kinetically different variants are possible.

1. Isotope exchange in molecular oxygen [reaction (1)] occurs without involving the oxygen of the catalyst. In this case $d\alpha/d\tau = 0$, and the change in concentration of $^{16}O^{18}O$ molecules is described by Eqn. (2).

2. Exchange in molecular oxygen involves one atom of oxygen from the catalyst. In this case

$$-\frac{d\alpha}{d\tau} = {}^1/_2 k_2(\alpha - \alpha_s) \quad (4)$$

and

$$\frac{dC_{34}}{d\tau} = k_2[\alpha(1-\alpha_s) + \alpha_s(1-\alpha) - C_{34}]. \quad (5)$$

3. Exchange in molecular oxygen involves two atoms of oxygen from the catalyst. In this case

$$-\frac{d\alpha}{d\tau} = k_3(\alpha - \alpha_s) \quad (6)$$

and

$$\frac{dC_{34}}{d\tau} = k_3[2\alpha_s(1-\alpha_s) - C_{34}]. \quad (7)$$

If the exchange occurs by all three mechanisms at the same time,

$$-\frac{d\alpha}{d\tau} = \left(\frac{k_2}{2} + k_3\right)(\alpha - \alpha_s) = R'(\alpha - \alpha_s) \quad (8)$$

$$\frac{dC_{34}}{d\tau} = k_1[2\alpha(1-\alpha) - C_{34}] + k_2[\alpha(1-\alpha_s) + \alpha_T(1-\alpha) - C_{34}] + k_3[2\alpha_s(1-\alpha_s) - C_{34}] \quad (9)$$

where $k_1 = Z_1S/N_g$, $k_2 = Z_2S/N_g$, $k_3 = Z_3S/N_g$, and Z_1, Z_2, Z_3 are the numbers of oxygen molecules (molecules cm^{-2} s^{-1}) which exchange atoms by the corresponding mechanisms.

Eqn. (9) can be recast[18] by inserting the value of α_s from Eqn. (8) and introducing the new variable

$$y = 2\alpha(1-\alpha) - C_{34} = C^*_{34} - C_{34}.$$

The physical significance of this variable is that of a driving force for the isotope exchange between oxygen molecules. In the absence of isotope exchange with the oxygen of the catalyst, the fractional change in the number of molecules would be proportional to y.

With this substitution, Eqn. (9) can be written in the form

$$\frac{dy}{d\tau} = -ky + \varphi\left(\frac{d\alpha}{d\tau}\right)^2 \quad (10)$$

where

$$\varphi = \frac{8k_3}{(k_2 + 2k_3)^2} \text{ and } k = k_1 + k_2 + k_3.$$

To solve the resulting system of differential equations we must know the variation of α_s with time of exchange. This variation can be quite complicated, because it is determined not only by the rate of exchange of surface oxygen atoms from the catalyst but also by the rate of diffusion of atoms which have been exchanged into the bulk of the catalyst. In its general form, the problem is soluble only in some special cases[18].

Generally speaking, the exchange constants k_1, k_2, k_3 can be evaluated by means of the differential equations (8) and (9) from experimentally found values of $d\alpha/d\tau$ and $dC_{34}/d\tau$ at different times. Reliable results can be obtained in this way only from a large number of measurements, which must be of the highest precision.

To characterise the role of the individual mechanisms, it is desirable to work with catalyst samples containing very small amounts of ^{18}O, whilst ensuring a high total concentration of this isotope in the molecular oxygen. Fig.1 shows the curves for the change in isotopic composition of the molecular oxygen, assuming different exchange mechanisms, for the case of $\alpha_s \ll \alpha$. If the concentration of the ^{18}O isotope in the enriched oxygen (from which the reaction mixture is prepared by dilution with ordinary oxygen) is in excess of 50%, we have $\alpha^0 > C^0_{34}$ at zero time. Hence it

is possible to identify the predominant exchange mechanism by the following qualitative rules:

a) if $\left(\frac{d\alpha}{d\tau}\right)_{\tau=0} = 0$, and $\left(\frac{dC_{34}}{d\tau}\right)_{\tau=0} > 0$, exchange occurs by mechanism *1*;

b) if $\left(\frac{d\alpha}{d\tau}\right)_{\tau=0} < 0$, and $\left(\frac{dC_{34}}{d\tau}\right)_{\tau=0} > 0$, mechanism *2* predominates;

c) if $\left(\frac{d\alpha}{d\tau}\right)_{\tau=0} < 0$, and $\left(\frac{dC_{34}}{d\tau}\right)_{\tau=0} < 0$, exchange occurs by mechanism *3*.

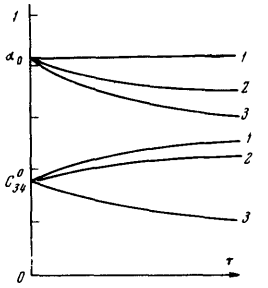


Figure 1. Change in isotopic composition of molecular oxygen for the different mechanisms of exchange. The numbers on the curves denote the exchange mechanism

Evidence for the third mechanism is provided also by a change in the ratio of the isotopic oxygen molecules (initially in homomolecular equilibrium) during exchange with oxygen from the oxide. If the exchange involves only the second mechanism ($k_3 = 0$), the homomolecular exchange equilibrium

$$\beta = \frac{C^2_{34}}{C_{32}\ C_{36}} = 4$$

will not be disturbed. Thus, if $k_3 = 0$, it follows that $\varphi = 0$, and from Eqn. (10) $dy/d\tau = 0$ under homomolecular equilibrium ($y = 0$).

Non-constancy of β during exchange is evidence that the exchange is occurring by the third mechanism.

All these conclusions involve the assumption of a uniform catalyst surface in respect of oxygen exchange. If the surface is not uniform, the constants k_1, k_2, and k_3 will vary from point to point on the surface. However, since exchange in this case will be confined to the most active regions of the surface, we can evaluate approximate exchange constants for these regions from experimental data for very small values of τ and $\alpha_s \ll \alpha$.

III. EXPERIMENTAL DATA ON ISOTOPE EXCHANGE IN MOLECULAR OXYGEN ON SOLID CATALYSTS

1. Catalytic Activity of Oxides

The influence of the conditions of pretreatment of oxides on their catalytic activity towards homomolecular oxygen exchange was first pointed out in Winter's review[3]. More recent work[14,16,24,29,31,33] has shown that in some cases the activity is greatly increased by a preliminary vacuum activation at high temperature, whereas oxygen treatment at high temperatures causes a sharp fall in activity. Some oxides showed differences in activity of several orders after different treatments. Since the change in activity caused by pretreatment under different conditions is evidently associated with a change in the oxygen content, it is desirable to compare the catalytic activity of the various oxides under two different headings: samples which have been treated in oxygen at a temperature high enough to ensure equilibrium composition of the surface layer, and samples having a non-equilibrium oxygen concentration in the surface layer.

2. Oxides with Equilibrium Oxygen Concentration in the Surface Layer

The main results (published since 1958) on the catalytic activity of oxides of equilibrium composition towards the isotope exchange reaction in molecular oxygen are summarised in Table 1. For comparison, the activity of platinum is also given in the Table.

Table 1. Kinetic characteristics of homomolecular exchange reactions of O_2 on various catalysts

Catalyst	Ranges of temp., °C	Ranges of oxygen pressure, mmHg	Surface area, $m^2\ g^{-1}$	Rate of exchange*, molecules $cm^{-2}\ s^{-1}$	Activation energy, kcal mole^{-1}	Pre-exponential factor, molecules $cm^{-2}\ s^{-1}$	Kinetic order with respect to oxygen	Literature references
Pt	200—250	0.15—0.5	0.4; 1.6	$6.7\cdot10^{13}$	16.5	$1.0\cdot10^{20}$	0.5	11
MgO	400—500	10	26	$1.8\cdot10^{7}$	40	$1.8\cdot10^{22}$	—	10
γ-Al_2O_3	400—500	10	190	$3\cdot10^{7}$	(32)	$3\cdot10^{19}$	—	10
TiO_2	530—600	40	67	$2\cdot10^{6}$	(39)	—	—	8
V_2O_5	450—550	5—240	2.7	$1\cdot10^{7}$	46	$1.9\cdot10^{24}$	0.7—0.8	6
Cr_2O_3	450—550	5—240	2.9	$6.1\cdot10^{7}$	42	$4.9\cdot10^{23}$	0.6—0.7	8
MnO_2	225—325	6—240	55	$2.1\cdot10^{12}$	22	$4.0\cdot10^{20}$	0.4	8
Fe_2O_3	350—450	6—240	27	$9.4\cdot10^{9}$	33	$2.7\cdot10^{23}$	0.6	8
Co_3O_4	125—250	4—240	7.7	$5.2\cdot10^{13}$	16	$5.2\cdot10^{19}$	0.4	8
NiO	225—300	5—120	7.7	$6.7\cdot10^{11}$	24	$6.7\cdot10^{20}$	0.4	8
CuO	250—350	4—240	18	$7.0\cdot10^{11}$	26	$3.9\cdot10^{21}$	0.4	8
ZnO	425—525	13—120	1.0	$3.7\cdot10^{8}$	40	$3.7\cdot10^{23}$	0.9	8
MoO_3	550—600	11—38	0.78	$2.6\cdot10^{8}$	69	$2.1\cdot10^{29}$	1.0	10
La_2O_3	400—450	20—40	28	$2.2\cdot10^{11}$	25	$7.0\cdot10^{19}$	1.1	28
CeO_2	320—420	14—80	29	$3.5\cdot10^{11}$	31	$1.2\cdot10^{23}$	1.0	28
Pr_6O_{11}	200—290	20—74	32	$4.4\cdot10^{13}$	20	$2.8\cdot10^{20}$	0.9	28
Nd_2O_3	200—300	6—80	26	$9.5\cdot10^{12}$	14	$5.6\cdot10^{17}$	1.1	28
Sm_2O_3	325—420	20—80	42	$1.1\cdot10^{12}$	14	$6.7\cdot10^{16}$	0.8	28
Gd_2O_3	300—370	20—80	31	$1.4\cdot10^{12}$	15	$1.8\cdot10^{17}$	1.1	28
Tb_4O_7	300—370	20—80	49	$2.8\cdot10^{12}$	24	$4.1\cdot10^{20}$	0.6	28
Dy_2O_3	326—420	20—84	49	$4.5\cdot10^{11}$	20	$2.9\cdot10^{17}$	0.9	28
Ho_2O_3	320—420	20—80	46	$3.8\cdot10^{11}$	25	$1.2\cdot10^{19}$	1.0	28
Er_2O_3	200—300	12—98	21	$3.1\cdot10^{13}$	18	$4.1\cdot10^{18}$	1.0	28
Tu_2O_3	300—420	20—80	22	$2.6\cdot10^{12}$	17	$1.5\cdot10^{18}$	1.0	28
Yb_2O_3	300—420	20—58	34	$2.6\cdot10^{11}$	20	$1.7\cdot10^{18}$	1.2	28
Lu_2O_3	300—420	20—80	20	$1.9\cdot10^{12}$	15	$2.5\cdot10^{17}$	1.1	28

* For MgO and γ-Al_2O_3 at 300°C and 10 mmHg, for the rare-earth oxides at 370°C and 20 mmHg, for the other catalysts at 300°C and 40 mmHg.

The oxides examined usually had a steady activity towards homomolecular exchange in oxygen, with the exception of NiO and CuO whose activity gradually fell to a stable value in 1–2 days[8]. Evidently, the conditions of treatment adopted had failed to ensure an equilibrium oxygen content in the surface layer of these oxides, and the achievement of phase equilibrium continued during the measurements of homomolecular oxygen exchange. The values listed in Table 1 refer to the stable activity of these oxides. The temperature dependence of the rate of exchange for a

series of oxides of the fourth period of the Periodic Table is shown in Fig. 2.

Some of the data listed in Table 1 differ from the results obtained by other workers. Thus, the rate of exchange observed by Winter[2] on NiO (from the carbonate) was approximately 100 times lower, and the activation energy was higher (35 kcal mole^{-1}). These discrepancies are probably due to different amounts of excess oxygen in the samples.

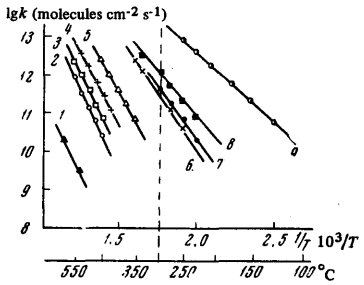


Figure 2. Temperature dependence of the rate of exchange of molecular oxygen on the oxides of metals from the fourth period: *1*) TiO_2; *2*) V_2O_5; *3*) Cr_2O_3; *4*) ZnO; *5*) Fe_2O_3; *6*) CuO; *7*) NiO; *8*) MnO_2; *9*) Co_3O_4.

The rate of exchange on Fe_2O_3 according to Winter[2] is close to the value given in Table 1, but the activation energy (19.2 kcal mole^{-1}) and the kinetic order with respect to oxygen (~ 1) are substantially different. According to Sazonov and coworkers[31], the activity of CeO_2 is approximately 40 times lower, and that of Gd_2O_3 4–8 times higher than Minachev and Antoshin's values[28], the activation energies being 31 and 10 kcal mole^{-1} respectively. These differences may be associated with the preparative conditions of the oxides. Sazonov and coworkers[27] studied the exchange in molecular oxygen on neodymium oxide, and found that the activity can vary by about an order of magnitude depending on the preparation and treatment conditions of the catalyst (E = 30 kcal mole^{-1}). The effect of the activation conditions on the catalytic activity towards homomolecular oxygen exchange, associated with a change in the oxygen content of the oxide, has been reported also for manganese dioxide[23].

Isotope exchange in molecular oxygen on oxides with an equilibrium oxygen concentration in the surface layer takes place in the temperature range where the surface oxygen has sufficient mobility and is able to exchange with the gas phase.

As regards their behaviour towards isotope exchange with the gas phase, the oxides investigated can be classified into the following groups.

1. Oxides in which the whole of the oxygen is equivalent. (The mobility of the oxygen in the lattice is greater than the rate of exchange with the gas phase.) This group includes V_2O_5,[39,40] CeO_2 [41] (oxygen diffusion in the CeO_2 lattice begins to affect the rate of exchange only above 440°C)[31], and MoO_3.

2. Oxides in which the surface oxygen has uniform mobility but exchange with the underlying layers of lattice oxygen is diffusion-limited. This group includes Fe_2O_3,[8,42] ZnO, Cr_2O_3,[8] Al_2O_3,[24] and the rare-earth oxides[41].

3. Oxides in which the surface oxygen is non-uniform towards isotope exchange with the gas phase. These are MnO_2,[42,43] Co_3O_4, NiO, and CuO.[8,42]

As an example, Fig. 3 shows the variation in the exchange rate as the fraction of exchangeable oxygen on the surface of MnO_2 is increased[23]. It is interesting to note that higher activation temperatures, which increase the activity of manganese dioxide towards oxygen isotope exchange, decrease the degree of non-uniformity of the surface oxygen. On raising the temperature of exchange the non-uniformity of the surface oxygen decreases.

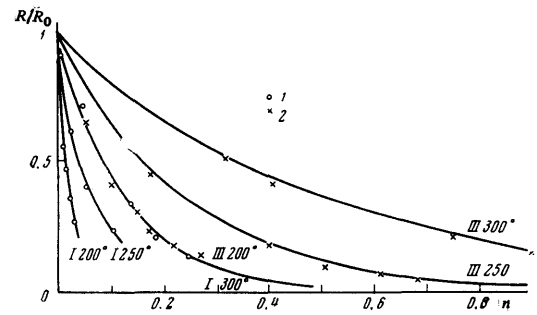


Figure 3. Decrease in the rate of exchange between O_2 and manganese dioxide with increase in the fraction of surface oxygen exchanged. The heat treatment temperatures were 350°C for preparation *I* (points *1*) and 550°C for preparation *III* (points *2*).

The NiO preparation investigated by Keier[44] showed uniformity of the surface oxygen, in contrast to the findings of other workers[8,42].

Winter[3] had noticed that on Cr_2O_3, NiO, and Fe_2O_3 the rates of exchange in molecular oxygen (Z) and of isotope exchange with the oxygen of the oxide (R) are closely similar. Subsequent work confirmed[8] that this behaviour is characteristic of all the oxides in which the equilibrium oxygen concentration is present. Results obtained[8] for transition metal oxides of the fourth period are listed in Table 2. The identity of the rates for the processes under discussion is particularly striking with the oxides in which the surface oxygen is uniform for isotope exchange with the gas phase (V_2O_5, Cr_2O_3, ZnO, Fe_2O_3). With these oxides the experimental values of the heteromolecular and homomolecular exchange rates agree within the limits of the inequality $R \leqslant Z \leqslant 2R$.

The rates of the exchange processes are more difficult to compare when the surface oxygen of the oxide is non-uniform and the rate of isotope exchange is lowered by confining the reaction to a monolayer. In this case the rate of exchange in molecular oxygen should coincide with the maximum initial rate of isotope exchange with the surface oxygen of the catalyst. Fig. 4 shows experimental results, obtained[23] on MnO_2, which support this argument. With Co_3O_4 a reliable determination of the initial rate of heteroexchange proved impossible.

Satisfactory agreement between the rates of hetero- and homo-molecular exchange was obtained also for the oxides CeO_2, Cd_2O_3, and Nd_2O_3.[27,31]

Several workers have examined the effect of various additives known to influence the semiconducting properties of the oxides on the rate of isotopic oxygen exchange.

Winter[2] studied oxygen exchange on NiO containing oxides of lithium, silver, and tungsten, and observed a rather weak correlation between the nature of the added oxide and the resulting change in rate. This may have been due to incomplete dissolution of the dopant at the low firing temperature used (650°C). According to Keier[44], the addition of 0.8 at. % of Li to NiO increased the exchange rate by a factor of 7–8 whilst the electrical conductivity rose by 5 orders of magnitude. The effect of the temperature at which the impurities are added to NiO was investigated by Gorgoraki and coworkers[29], who found that Li and In impurities added to NiO at 800°C had practically no effect on the activation energy: with the addition of lithium the reaction rate increases, but with the addition of indium it remains practically unaffected. Increasing the firing temperature of the preparation containing indium from 800° to 1200°C led to a sharp drop in reaction rate, possibly as a result of more complete dissolution of the impurity. Raising the firing temperature of pure NiO from 800° to 1200°C causes a slight drop in rate and an increase in the apparent activation energy of the exchange reaction.

Table 2. Comparison between rates of exchange in molecular oxygen and rates of isotope exchange with the oxygen of the oxide.

Oxide	Temp., °C	Rate of exchange, molecules $cm^{-2}\ s^{-1} \times 10^{-11}$	
		in molecular oxygen	with the oxygen of the oxide
V_2O_5	550	13.6	13.1
	550	2.4	1.7
Cr_2O_3	525	16.7	16.7
	400	0.31	0.63
ZnO	500	29.0	15.0
Fe_2O_3	400	6.8	4.7
NiO	300	6.8	6.8
CuO	300	5.7	4.7
MnO_2	300	21.0	25.0
	250	3.2	3.1

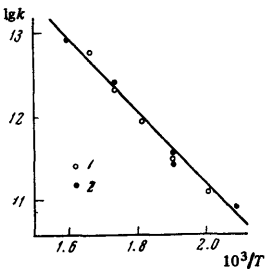


Figure 4. Comparison of the rates of exchange in molecular oxygen with the initial rates of exchange between O_2 and MnO_2: *1*) exchange in molecular oxygen; *2*) exchange with the oxygen of the oxide.

Gorgoraki and coworkers[12,13,45] studied the effect of Li, Ga, and In impurities on the activity of ZnO. Additions of lithium were found to increase the activity, whereas indium and gallium additions lowered it.

Margolis and Kiselev[5] studied the effect of adding the oxides Cr_2O_3, Bi_2O_3, and Li_2O to copper oxide.

Alkali metal sulphates are used as promoters in a variety of industrial vanadium catalysts[46]. Studies of the effect of alkali metal salts on the activity of V_2O_5 towards the isotope exchange of oxygen have shown that the mobility of oxygen in vanadium pentoxide is appreciably raised by alkali metal compounds[6,34,47-49]. As in the case of V_2O_5, volume diffusion of oxygen in the bulk of the promoted catalysts is much faster than the surface exchange. It is interesting to note that the promoted samples show very fast oxygen exchange not only of the vanadium pentoxide, but also of the impurity, whereas the oxygen of alkali metal salts does not in any way exchange with molecular oxygen under comparable conditions. The rates of hetero- and homo-molecular oxygen exchange on promoted vanadium pentoxide catalysts were found to be very similar[6].

Kasatkina and Antoshin[15] studied the isotope exchange between O_2 and CO_2 molecules and the heteroexchange of MnO_2 with O_2 and CO_2 on manganese dioxide which had been activated in a vacuum at 350°C. They found that the exchange of oxygen atoms between CO_2 molecules on the surface of manganese dioxide is much faster than reaction (1). The oxygen of MnO_2 proved to be very non-uniform towards exchange with CO_2: the first experimental points were obtained at extents of exchange of 8–16% of a monolayer, at which the rate of exchange is several times lower than the maximum. Later work from the same laboratory[23] showed that the rate of exchange of CO_2 with MnO_2, like the rate of exchange of O_2 within the limits of a monolayer, decreases exponentially as the extent of exchange increases. The initial rates of exchange of oxygen between CO_2 and MnO_2 calculated from the exponential law were identical to the rate of isotope exchange in molecular CO_2. The rate of isotope exchange between O_2 and CO_2 was much lower than the rate of isotope exchange between CO_2 and MnO_2, and was somewhat lower than (but of the same order as) the rate of exchange between O_2 and MnO_2. These results justify the conclusion that exchange between O_2 and CO_2 occurs through the exchange of these gases with the oxygen of the manganese dioxide surface, and that the exchange of molecular oxygen is the rate-limiting step.

Kiyoura[50] subsequently arrived at the same conclusions by studying the exchange between O_2 and CO_2 on the oxides TiO_2, V_2O_5, Cr_2O_3, Fe_2O_3, NiO, MnO_2, and Co_3O_4 at 150–600°C. On all these oxides the rate of exchange decreased in the sequence: CO_2–oxide > O_2–oxide > O_2–CO_2 (on the oxide).

Exchange between CO_2 and O_2 was observed only when exchange between molecular oxygen and the oxide was possible.

3. Basic Features of Exchange in Molecular Oxygen on Oxide Catalysts with Equilibrium Oxygen Content

a. Exchange mechanism. In view of the close similarity between the rates of homomolecular oxygen exchange and of isotopic exchange with the oxygen of the oxide, we may conclude that the simplest catalytic reaction—isotope exchange in molecular oxygen—occurs with participation of the oxygen from oxides with an equilibrium oxygen content. If the oxide has a uniform surface, the whole of the surface oxygen takes part in the reaction, but if the oxide surface is non-uniform, only the most active ("mobile") oxygen atoms are involved. Hence, of the possible exchange mechanisms discussed above, mechanism *1* is excluded for oxides with an equilibrium oxygen content. It is harder to establish whether isotope exchange in molecular oxygen occurs on these oxides by mechanism *2* or

by mechanism *3*, that is, whether one or two oxygen atoms from the catalyst are involved. The problem may be solved using an analysis of the exchange kinetics for the various mechanisms given above (p. 614).

Dzisyak and coworkers[8] have established qualitatively, from the time-changes of the quantity C_{34}/C_{36}, that exchange on V_2O_5 and on V_2O_5 doped with alkali metal sulphates occurs mainly with the participation of two oxygen atoms from the catalyst. Jiru and Novakova[34] independently reached the same conclusion for those catalysts.

Muzykantov and coworkers[19] quantitatively assessed the rates of exchange on V_2O_5 by different mechanisms by studying the exchange between V_2O_5 and oxygen of normal isotopic composition ($y_0 = 0$). They observed the change in the value of y with time of exchange (Fig. 5*a*), and found that y goes through a maximum when plotted against τ. By measuring $dy/d\tau$ at $\tau = 0$ and y_{max} from the experimental curves, the values of k_3 and k can be calculated[18]. Thus, substituting into Eqn. (10) the value of $d\alpha/d\tau$ from Eqn. (3), and assuming $y_0 = 0$, we obtain

$$k_3 = \frac{\left(\frac{dy}{d\tau}\right)_{\tau=0}}{2(\alpha^0 - \alpha^*)^2}\left(\frac{N_s}{N_g + N_s}\right)^2.$$

At the maximum, $dy/d\tau = 0$, and

$$k = \frac{\left(\frac{dy}{d\tau}\right)_{\tau=0}}{y_{max}\, e^{2r\tau}}, \text{where } r = \frac{N_g + N_s}{N_g N_s} SR.$$

Table 3. Homomolecular exchange of oxygen with simultaneous heteromolecular exchange between O_2 and V_2O_5.

Temperature, °C	p_{O_2}, mmHg	y_{max}, %	τ_{max}, min	R, molecules cm^{-2} s^{-1}	Z_3, molecules cm^{-2} s^{-1}	Z_3/Z
450	11	—	—	$4.6\cdot10^8$	$4.6\cdot10^8$	—
462	11	—	—	$1.1\cdot10^9$	$1.1\cdot10^9$	—
475	11	5.5	620±40	$1.9\cdot10^9$	$1.9\cdot10^9$	0.9—1.0
483	11	5.3	400±30	$2.5\cdot10^9$	$2.4\cdot10^9$	0.7—0.8
500	11	5.5	200±20	$5.1\cdot10^9$	$5.1\cdot10^9$	0.9—1.0
500	31	5.5	400±30	$7.8\cdot10^9$	$7.8\cdot10^9$	0.9—1.0
500	46	5.4	470±30	$9.6\cdot10^9$	$9.6\cdot10^9$	0.9—1.0

The results of this work are set out in Table 3. We can see that $Z_3 = R = Z$, i.e. $Z_2 = 0$ and $Z_1 = 0$, and therefore the exchange between molecular oxygen and the oxygen of vanadium pentoxide consists in the replacement of two atoms from the gas-phase molecule undergoing exchange by two atoms from the surface layer of the oxide. The observed rate of exchange is equal to the rate of the reversible surface dissociation of the oxide with formation of molecular oxygen.

Minachev and Antoshin[28] also observed, for all the oxides of the rare-earth elements except thulium and lutetium oxides, a departure from equilibrium in the gas phase during exchange with oxygen of equilibrium isotopic composition. Therefore, on these oxides also, exchange in molecular oxygen mainly involves two atoms of oxygen from the oxide in the elementary exchange act. The values of R, calculated for various oxides from the variation of α with τ, and of k_3, from data on the variation of y with τ during exchange on the same oxides (Fig. 5*b*), are very similar.

An unambiguous choice between mechanisms *2* and *3* cannot yet be made for the majority of oxides, due to lack of sufficiently accurate data. However, the similarity between the rates of exchange in molecular oxygen and of isotope exchange with the oxygen of the oxide is evidence that exchange on oxides of equilibrium oxygen content involves the participation of oxygen from the oxide, and therefore the rate of exchange should be a function of the energy and of the nature of the oxygen bond in the surface layer of the oxide.

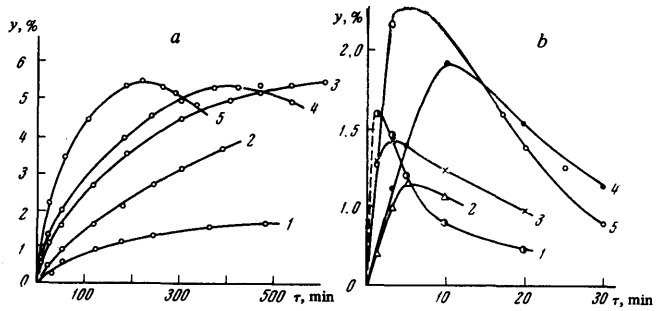


Figure 5. Variation of the quantity y with time of exchange; *a*) on V_2O_5 at 11 mmHg oxygen pressure, temperature (°C):
1) 450; *2*) 463; *3*) 475; *4*) 483; *5*) 500;
b) on rare-earth oxide at 370°C and 40 mmHg:
1) Nd_2O_3; *2*) Ho_2O_3; *3*) Dy_2O_3; *4*) CeO_2; *5*) CeO_2 (420°C).

b. Relationship between the catalytic activity towards exchange in molecular oxygen and other properties of the oxide. The oxygen bond energy in the surface layer of the oxide is uniquely determined by the electronic structure of the metal atom. Unfortunately, neither computational nor experimental methods of determining this energy are yet available. If, as a very rough approximation, the heat of formation per oxygen atom computed from thermodynamic data is used, the activation energy for the exchange reaction on oxides of metals from the fourth period is found to change monotonically with this quantity (see Fig. 6). The optimum bond energy corresponds to cobalt oxide, whereas in copper oxide the bond energy is apparently below the optimum.

On this basis, the study of oxides of metals from the fourth period can be divided into two groups. The oxides of the first group, including TiO_2, V_2O_5, Cr_2O_3, Fe_2O_3, and ZnO are characterised by a high bond energy, relatively low activity, and high activation energy for the exchange reaction. The kinetic order of the reaction with respect to oxygen is 0.6–0.8; the surface oxygen is uniform. All these oxides (except Cr_2O_3) are weakly semiconducting (*n*-type). The conductivity of chromic oxide is not yet clearly characterised: according to some measurements, this oxide exhibits *p*-type semiconductor properties after heat treatment in oxygen. For most of the oxides in this group, the number of electrons in the 3*d* shell of the cations corresponds to the most stable configuration: 0 for TiO_2 and V_2O_5, 5 for Fe_2O_3, and 10 for ZnO.

The second group comprises the oxides of lower oxygen bond energy: Co_3O_4, NiO, CuO, and MnO_2. On these oxides the exchange is fast, and is characterised by a low activation energy and a low pre-exponential factor. The order of the reaction is 0.3–0.4. The surface oxygen is not energetically uniform. The oxides of the second group,

on the whole, are *p*-type semiconductors of relatively high conductivity. The number of electrons in the 3*d* shell of the cations is 3 for MnO_2, 7 and 8 for Co_3O_4, 8 for NiO, and 9 for CuO.

The more active the oxide, the lower are the observed activation energy and pre-exponential factor. On going from the most active catalyst (Co_3O_4) to the relatively inactive V_2O_5, the activation energy increases by 30 kcal mole^{-1}, and the pre-exponential term increases by more than 4 orders of magnitude.

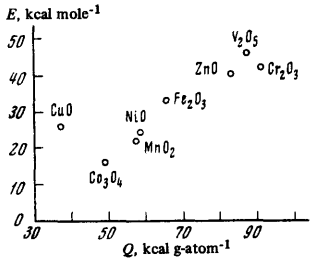


Figure 6. Correlation between the activation energy (E) for oxygen exchange on the oxides of fourth period metals and the heat of formation (Q) of the oxide referred to 1 g-atom of oxygen.

Winter noted breaks in the linear Arrhenius plots for the isotope exchange of oxygen with MgO [51] and ZnO [52], and for the homomolecular oxygen exchange on Cr_2O_3 [2] and on NiO from $Ni(NO_3)_2$.[3] These breaks correspond to a substantial decrease in activation energy at high temperatures. In our work[8], no such decrease in activation energy could be observed in the high-temperature region. Possibly, the drop in activation energy observed by Winter at high rates of exchange may have arisen from the onset of diffusional control, which was excluded in our work[8] by forced circulation of the reaction mixture.

Assuming that the rate-limiting step in the exchange is oxygen sorption (over the entire surface of the oxide), and that the active sorption complex is delocalised, the theory of absolute reaction rates[53] leads to the following value of the pre-exponential factor

$$k_0 = C_g \sqrt{\frac{kT}{2\pi m}}$$

where C_g is the concentration of sorbed molecules (cm^{-3}), k is Boltzmann's constant, and m is the mass of the molecule (grammes).

The maximum possible value of k_0 for the conditions corresponding to the data in Table 1 is 10^{22} molecules cm^{-2} s^{-1}. If the activated complex on the surface is localised, the theoretical value of the pre-exponential factor decreases. The loss of the translational degrees of freedom for motion along the surface and of the rotational degrees of freedom of the active complex lowers the theoretical value of k_0 by almost five orders of magnitude.

If desorption (again, over the entire surface) is rate-limiting, the maximum theoretical value of the pre-exponential factor rises to 10^{28} molecules cm^{-2} s^{-1}.

The experimental results listed in Table 1 show that the pre-exponential factor for the oxides of the first group is much greater than the maximum possible value for the rate of adsorption. Hence, we must conclude that the observed activation energy for the exchange is much higher than the activation energy for adsorption, and approaches the activation energy for desorption. Thus, for V_2O_5 the true activation energy for adsorption should be lower than the observed activation energy for exchange by at least 10 kcal mole^{-1}, in order to bring the value of k_0 below the theoretical maximum. This means that the surface of these oxides is effectively covered by oxygen, and oxygen removal is the rate-limiting step. This argument is supported by the fact that the rate of exchange on V_2O_5 was found to be approximately equal to the experimentally observed desorption rate.

In oxides of the second group the surface is, apparently, largely free to adsorb oxygen, and the observed activation energy for exchange is close to the true activation energy for sorption. The low value of the pre-exponential factor (as compared with the theoretical maximum) is probably the result of non-equivalence of the surface oxygen on these oxides. The degree of non-uniformity of the surface oxygen increases in the order $CuO < NiO < MnO_2 < Co_3O_4$. Hence it must be assumed that exchange in molecular oxygen occurs only on part of the surface of these oxides, the fraction of the surface involved being smaller, the greater the degree of non-uniformity. This explains the decrease in the pre-exponential factor on going from CuO to Co_3O_4. Low k_0 values may also arise from localisation of the active oxygen sorption complex.

These ideas on the relationship between the rate of exchange in molecular oxygen and the oxygen bond energy on the surface of the oxide can also be applied to the action of promoters in vanadium pentoxide. The addition of alkali metal sulphates to V_2O_5 leads to the formation of compounds close in composition to $V_2O_5.M_2SO_4$ and soluble in the excess of vanadium pentoxide. The oxygen bond energy in the resulting solid solutions is lowered, and therefore the activation energy decreases and the rate of exchange in molecular oxygen increases. The mobility of the oxygen increases, depending on the alkali metal, from lithium to caesium: in other words, the oxygen bond energy in a series of promoted catalysts changes monotonically with the atomic number of the alkali metal. As shown in Fig. 7, the rate and the activation energy of exchange on vanadium pentoxide promoted by alkali metal sulphates vary in the same sense as the electronegativity[54] of the alkali metal atom.

From Minachev and Antoshin's data[28], the change in the mobility of oxygen in the rare-earth oxide family is similar in character to the change in energy of the oxygen bond in the oxides. Inspection of Table 1 shows that the pre-exponential factor for these oxides is less than 10^{22} (with the exception of CeO_2). With CeO_2, the rate-limiting step in the exchange is apparently oxygen sorption over the entire surface of the oxide. The non-stoichiometric oxides of praseodymium and terbium, characterised by high concentrations of oxygen defects in the lattice, are the most active. Under exchange conditions all these oxides (except CeO_2) are *p*-type semiconductors.

c. Activity towards isotopic exchange of oxygen and semiconducting properties of oxides. During isotope exchange on oxides with equilibrium oxygen content, mutual transformations of molecular oxygen and atomic oxygen ions, involving electron transfer, must take place. Therefore, the electronic work function can be one of the terms which define the value of the activation energy for the exchange reaction. It is interesting

to establish whether a relationship exists between the catalytic activity towards isotope exchange in oxygen and the electronic work function. Experimental results[9] for a series of transition metal oxides are given in Table 4.

The activity was characterised by the rate of exchange at 300°C, and the work function by the contact potential difference between the oxide and gold[55]. The data of Table 4 suggest the lack of a simple correlation between catalytic activity and work function. For comparable values of the work function the catalytic activities of some oxides differ by five orders of magnitude, and for the same activity the work function can vary by more than 1 eV. It follows that the change in work function between different oxides is neither the only nor the main factor which determines the catalytic activity.

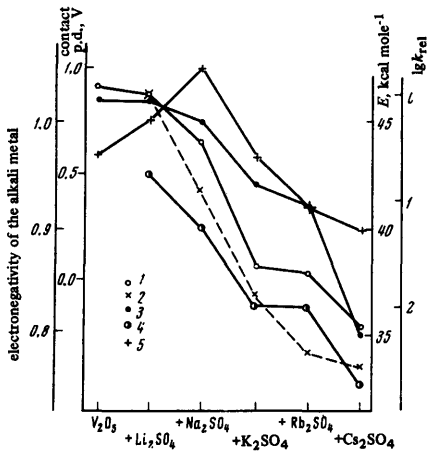


Figure 7. Activity of vanadium pentoxide promoted by alkali metal sulphates:
1) logarithm of the relative rate of exchange in molecular oxygen ($\lg k_{rel}$); *2*) logarithm of the relative rate of oxidation of SO_2 ($\lg k_{rel}$); *3*) activation energy of exchange (E); *4*) electronegativity of the alkali metal atom; *5*) electronic work function (contact p.d.).

Table 4. Catalytic activity and electronic work function of the oxides of metals of the fourth period.

Oxide	Contact potential difference against gold, V	Exchange rate at 300°C, molecules $cm^{-2}\ s^{-1} \times 10^{-10}$
TiO_2	−1.36	0.0002
V_2O_5	−0.75	0.001
Cr_2O_3	−0.10	0.0061
Fe_2O_3	−0.74	0.94
Co_3O_4	−0.13	5200
NiO	+1.02	68
CuO	−0.03	70
ZnO	0.0	0.037

In promoted oxides, also, the electronic work function bears no simple relationship to the catalytic activity towards oxygen exchange. Thus, the addition of 0.5 at. % of lithium or gallium to zinc oxide has the same effect on the work function (which is lowered in both cases), but the catalytic activity of zinc oxide is increased by a factor of 4 by the addition of lithium and is decreased by a factor of 5 by the addition of gallium[12].

Addition of alkali metal sulphates to vanadium pentoxide raises both the catalytic activity and the electrical conductivity[48]. Promotion with the sulphates of different alkali metals does not correlate with the change in electronic work function (see Fig. 7). Addition of 0.1 M potassium sulphate to vanadium pentoxide increases 50-fold the rate of isotope exchange in oxygen, but has no significant effect on the electronic work function.

4. Catalytic Activity of Oxides with Non-equilibrium Oxygen Content

Many workers[14,16,24,29-31,33] have found that the activity towards homomolecular oxygen exchange is very considerably increased by preliminary activation of the oxides in a vacuum. The effect was first noted on zinc oxide. Samples of zinc oxide which have been heated in oxygen before measurements of their catalytic activity show appreciable activity only at temperatures above 400°C. At 450°C, and 40 mmHg oxygen pressure, $Z = 4.8 \times 10^{11}$ molecules $cm^{-2}\ s^{-1}$.

Winter[1] studied the activity of ZnO after vacuum activation for 16 h at 630°C, the oxygen being admitted after the sample had been cooled to the temperature of the experiment. Under these conditions, exchange in molecular oxygen is detectable even at 120°C, and at 215°C the rate of exchange reached 8×10^9 molecules $cm^{-2}\ s^{-1}$. Barry and Stone[33] obtained even more striking results: one of their zinc oxide preparations had an activity of 8.1×10^{11} molecules $cm^{-2}\ s^{-1}$ at −193°C.

A detailed investigation of the low-temperature activity of zinc oxide[16] has shown that exchange on freshly activated preparations proceeds to equilibrium almost instantaneously at 25° and −194°C, but even after 2–2.5 min the rate of exchange drops to a measurable level (5.7×10^{13} at 25° and 4.34×10^{10} molecules $cm^{-2}\ s^{-1}$ at −194°C). After 5–8 h operation in oxygen at room temperature the rate of exchange becomes immeasurably low.

Exchange on copper oxide vacuum-activated at 400°C occurs with initial rates too high for accurate measurement between 0° and −78°C. Cuprous oxide heated in vacuum at 400°C is active towards isotope exchange in molecular oxygen over the wide temperature range between −196° and +200°C: at all temperatures the rate of exchange decreases with time, reaching a constant value after 20–60 min. The initial rate of exchange at 25°C is 1.5×10^{12} molecules $cm^{-2}\ s^{-1}$.

The rate of exchange on NiO [14,29] was 1.2×10^{13} molecules $cm^{-2}\ s^{-1}$ immediately after activation, decreasing by about a factor of 3 after 27 h.

Manganese dioxide[30] baked in vacuum at 350°C shows a stable activity over a fairly long period in the temperature range from −78° to +50°C. The rate of exchange at 25°C on MnO_2 is 2.1×10^{12} molecules $cm^{-2}\ s^{-1}$. The activation energy in this temperature region is 3.7 kcal $mole^{-1}$, the kinetic order with respect to oxygen is 0.64. From 50°C upwards the rate of exchange decreases appreciably with time, eventually reaching the value typical of manganese dioxide stored in oxygen. The decrease in exchange rate is faster at higher temperatures. The temperature dependence of the rate of exchange on MnO_2 is shown in Fig. 8*a*.

The deactivation of these oxides in oxygen at low temperatures is reversible: repeated vacuum activation at high temperatures fully restores the low-temperature activity. Exchange at high temperatures on ZnO produces an irreversible deactivation of the catalyst towards exchange at low temperatures[16]. The low-temperature ac-

tivity of MnO_2 is fully restored by vacuum activation irrespective of the deactivation temperature[30]. In the case of CuO, further activation after high-temperature exchange produces a decrease in the rate of exchange at low temperatures, i.e. the activity is not fully recovered.

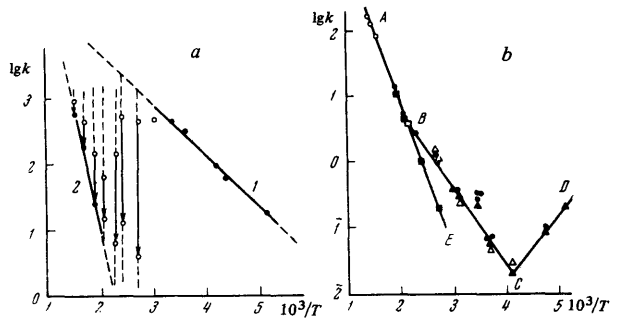


Figure 8. Temperature variation of the exchange rate in molecular oxygen; *a*) on MnO_2: *1*) with non-equilibrium oxygen content; *2*) with equilibrium oxygen content (open circles) and stable activity (filled circles), the unstable activity depending on the time of exposure of the catalyst to oxygen; *b*) on Gd_2O_3; *AE* high-temperature exchange on the oxide heated in oxygen, *BC* and *CD* low-temperature exchange on the oxide heated in a vacuum.

These results suggest the possibility of exchange by two different mechanisms, depending on the bond strength of the adsorbed oxygen to the oxide surface. Low-temperature exchange occurs only on catalysts which have been activated in a vacuum, i.e. under conditions when the oxide surface is strongly depleted of oxygen. This exchange does not involve participation of oxygen from the oxide: there is no isotopic exchange of oxygen between the oxide and the gas at low temperatures. Weakly adsorbed oxygen is probably involved. Exchange rates are high, and the activation energy low. Weakly adsorbed oxygen becomes more firmly bound, in time, to the surface of a vacuum-baked catalyst. This is accompanied by a decrease in the activity towards exchange by the low-temperature mechanism. The deactivation process is slow at low temperatures and fast at high temperatures. Therefore, the activity observed at high temperatures (even immediately after activation) corresponds to an oxide of surface composition close to—if not equal to—the equilibrium oxygen content. Under these conditions, isotope exchange between oxygen from the oxide and the gas takes place in parallel with homomolecular exchange. The rates of these processes are similar, and in this case the exchange in molecular oxygen proceeds through exchange with the oxide lattice. In the transition region of temperatures it is obviously possible, depending on the time of storage of the catalyst in oxygen, to observe homomolecular exchange at rates close to the rates characteristic of the low-temperature mechanism, or alternatively at rates close to those characteristic of the high-temperature mechanism.

The oxides of the rare-earth elements also show a low-temperature activity[31]. It is interesting to note that below 200°C the catalytic activity of gadolinium oxide heated in vacuum at 700°C for 4 h and rapidly cooled to room temperature remained stable even after prolonged storage (100 h) in oxygen at 20°C. The reproducibility of the measurements was adequate over the whole temperature range from −78° to +200°C and in both directions of temperature change. The low-temperature catalytic activity of the oxide began to change only after the catalyst had been heated in oxygen above 200°C, i.e. concurrently with the onset of isotope exchange between the gas phase and oxygen from the oxide. The temperature dependence of the activity of gadolinium oxide towards the isotope exchange of oxygen is illustrated in Fig. 8*b*. The presence of a break in the Arrhenius plot shows that the exchange can occur by different mechanisms, and the "negative" activation energy is evidence that the rate of exchange in the region *CD* is determined by the concentration of adsorbed oxygen, which increases with decrease of temperature.

Some interesting results have been obtained for γ-Al_2O_3.[17,24] The sample was prepared by thermal decomposition of the hydroxide followed by 10 h baking in air at 700°C. Exchange in molecular oxygen began at 350°C on a sample freshly prepared in this way. Vacuum treatment raised the activity of the catalyst, the effect increasing with temperature. Under these conditions, exchange was observed at temperatures as low as −78°C. The initial rates of exchange at 25°C and 10 mmHg oxygen pressure for various activation temperatures are tabulated below;

t, °C	300	350	400	450	500	600
Z_0, molecules $cm^{-2}\,s^{-1}$	0	$2\cdot10^{10}$	$3.5\cdot10^{10}$	$\sim10^{11}$	$5\cdot10^{11}$	$>10^{12}$

In an oxygen atmosphere the low-temperature activity of a vacuum baked sample decreases, rapidly at first and then slowly, reaching a stable value after 2–3 days: the rate is then 2–3 orders of magnitude less than the initial rate. Studies of the effects of temperature of heat treatment and of poisoning by water vapour on the activity of γ-Al_2O_3 lead to the conclusion that the active centres include sites remaining on the surface after removal of the OH groups[24].

Isotope exchange of molecular oxygen with oxygen from the oxide becomes appreciable in this case at a temperature of ~ 350°C, which is the same as the minimum activation temperature of γ-Al_2O_3 for low-temperature exchange in molecular oxygen, but the rate of hetero-exchange is approximately two orders of magnitude lower than the rate of homomolecular exchange. The whole of the oxygen on the surface of γ-Al_2O_3 takes part in hetero-exchange, whereas the active regions for homomolecular exchange occupy only a small fraction of the surface. These localised areas differ from the surface oxygen atoms which take part in exchange, as shown by the different response of the rates of hetero- and homo-molecular exchange to the conditions of pretreatment. Thus, increasing the degree of dehydration of γ-Al_2O_3 raises the rate of homomolecular exchange much more drastically than the rate of hetero-exchange, whereas oxygen treatment decreases the rate of homomolecular exchange but increases the rate of hetero-exchange[56].

Since there is no departure from homomolecular equilibrium following isotope exchange between molecular oxygen and the oxygen of γ-Al_2O_3 (i.e. $y = 0$), we conclude that hetero-exchange in this case involves the replacement of one atom from an adsorbed oxygen molecule by one oxygen atom from the surface layer of the oxide. A quantitative treatment of the experimental results for isotope exchange at 450°C indicates the following relative amounts of the various types of exchange: $k_1 = 0.95$, $k_2 = 0.05$, $k_3 = 0$.[24]

In every case, the high activity of the oxides at low temperatures arises from the formation of chemical defects at the oxide surface. In most cases these defects result from the loss of oxygen, and disappear after high-temperature treatment in oxygen. On γ-Al_2O_3 the active regions

can be of at least two types[56]: the first are formed by the loss of oxygen from the surface layer of the lattice during high-temperature treatment in a vacuum, and are poisoned by oxygen; the second are formed by the extensive dehydration of the surface during high-temperature treatment in a vacuum and in oxygen alike, and are stable to oxygen treatment but are rapidly poisoned by water vapour.

Isotope exchange of molecular oxygen on oxides which are active at low temperatures is not accompanied by isotope exchange with the oxygen of the oxide. This means that under these conditions the exchange does not involve the participation of oxygen from the oxide surface, i.e. the exchange proceeds exclusively by the first mechanism. It may take the form of dissociative adsorption and desorption, or the formation on the surface of a triatomic or tetratomic activated complex from one or two oxygen molecules. There are as yet no data on which to base a choice between these variants.

5. Catalytic Activity of Metals towards Molecular Oxygen Exchange

The isotope exchange of oxygen on metals was first investigated by Margolis[4]. Exchange was observed at 320°C on platinum after prolonged oxygen treatment at 300–400°C, and at 220°C on silver.

Margolis and Kiselev[5] examined the effect of chloride and iodide impurities in silver. On increasing the chloride concentration from 0.0015 to 0.015%, i.e. by a factor of 10, the rate of exchange fell by a factor of 3. Addition of iodine increased the rate of exchange of molecular oxygen.

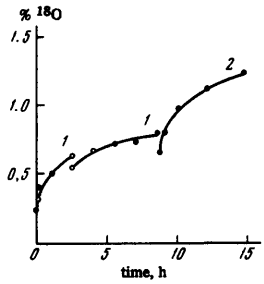


Figure 9. Isotopic exchange of molecular oxygen with oxygen adsorbed on platinum:
1) 200°C; *2*) 250°C.

Khasin and Boreskov[11] studied isotope exchange in oxygen on platinum films prepared by evaporation of platinum in a vacuum. The adsorption of oxygen on the freshly prepared films was measured at first, and found to include a fast stage and very slow stage. At 20°C the fast adsorption reached a coverage of 0.6×10^{15} atoms cm^{-2}, i.e. about half a monolayer, and at 250°C the amount of fast adsorption was in excess of a monolayer. Slow adsorption of oxygen took place throughout the experiment. The total amount of oxygen sorbed before starting the exchange experiments was 2–4 monolayers.

Even at 200°C the homomolecular exchange of oxygen on a platinum film occurs at a measurable rate. The activation energy of the exchange is 16.5 ± 1.5 kcal $mole^{-1}$. The kinetic order of the exchange reaction with respect to oxygen is close to 0.5.

The same films were used to study the exchange between adsorbed and molecular oxygen. Oxygen enriched with the heavy isotope (38% ^{18}O) was first adsorbed, the reaction vessel was filled with oxygen of normal isotopic composition, and the concentration of ^{18}O in the gas phase was monitored. The results are shown in Fig. 9. The discontinuities in the curve are due to the addition of natural oxygen to maintain the desired pressure, since the pressure is continually lowered by the removal of samples for analysis. The shape of the curves indicates a sharp decrease in exchange rate at low extents of exchange (below 0.1 of a monolayer), pointing to non-uniformity of the adsorbed oxygen.

The rate of exchange in molecular oxygen is the same as the maximum rate of exchange with adsorbed oxygen. The activation energy for exchange with adsorbed oxygen at an extent of exchange of 0.15 of a monolayer amounts to 28 ± 3 kcal $mole^{-1}$. Assuming appreciable non-uniformity of the adsorbed oxygen, the change in activation energy ΔE for the exchange with time τ can be calculated from the equation[57,58]

$$\Delta E = 2.3RT\,\Delta \lg \tau .$$

Fig. 10 shows the variation of the change in activation energy for exchange, measured in this way, with the extent of exchange x, defined as the fraction of a monolayer of adsorbed oxygen which has come to isotopic equilibrium with the gas phase. The dashed part of the curve is the extrapolation to $x = 0$. The results obtained justify the conclusion that oxygen adsorbed on a platinum film is non-uniform, and that the activation energy attending its exchange increases by 6 kcal $mole^{-1}$ over 25% of a monolayer. On the regions where homomolecular exchange takes place, the heat of adsorption of oxygen is ~ 13 kcal $mole^{-1}$, increasing to 28 kcal $mole^{-1}$ over 25% of a monolayer.

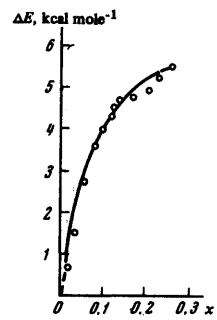


Figure 10. Change in the activation energy E for exchange of oxygen adsorbed on a platinum film with the extent of exchange x.

The exchange reaction in molecular oxygen occurs preferentially at zones which constitute ~ 3% of the total surface area of the platinum film. The higher rate of exchange of molecular oxygen found in this work (as compared with the results of Margolis[4]) is probably due to higher purity of the surface of the platinum film.

Subsequently[20–22], the homomolecular exchange of oxygen was studied on films of silver, palladium, and gold. It was shown that the rate of isotope exchange on palladium films is substantially decreased by oxidation of the metal,

pointing to a strengthening of the bond between adsorbed oxygen and the surface. Oxygen adsorbed on palladium films is energetically non-uniform. The bulk of this oxygen is barely mobile at 250°C, and is bound to the surface more firmly than in the case of silver. However, a very small fraction of the surface oxygen (< 2% of a monolayer) is very reactive towards exchange and plays a major role in the homomolecular isotope exchange reaction.

Oxygen adsorbed by a silver film at temperatures ≤ 200°C, and not exposed to higher temperatures, is uniformly accessible to exchange with gaseous oxygen at 200°C, suggesting that this oxygen is energetically uniform and has a high mobility. At 250°C part of this oxygen is transferred to a state which does not take part in exchange at 200°C: this state is characterised by a stronger bond to the silver.

Homomolecular exchange in oxygen on a gold film was negligible at 350° and 400°C. [22]

Comparative data for platinum, palladium, and silver are listed in Table 5. The difference in the interaction of oxygen with platinum and palladium surfaces on the one hand, and with silver surfaces on the other hand, evidently stems from the presence of *d*-orbitals in the first two metals, which can take part in bond formation with oxygen, whereas these orbitals are absent in silver [22].

Table 5. Comparison of the state of oxygen on films of platinum, palladium, and silver.

Metal	Rate of exchange at 250°C, Z^*, molecules $cm^{-2}\ s^{-1}$	Fraction of the surface involved in exchange, x	$\frac{Z}{x}$	Heat of adsorption of oxygen, kcal mole^{-1}	Activation energy of exchange, kcal mole^{-1}	Kinetic order with respect to oxygen
Pt	$7.83 \cdot 10^{12}$	~0.03	$\sim 1.96 \cdot 10^{14}$	13	16±2	0.5
Pd	$4.22 \cdot 10^{11}$	<0.02	$> 2.11 \cdot 10^{13}$	—	27—32	0.3
Ag	$2.41 \cdot 10^{12}$	~1	$\sim 2.41 \cdot 10^{12}$	13	29—34	0.3

* Values of Z obtained at 0.5 mmHg oxygen pressure on Pt, 0.1 mmHg on Pd and Ag.

Sandler and Durigon [35] studied the homomolecular exchange and adsorption of oxygen on spongy silver, and found that at 160–180°C the chemisorption of oxygen is partially reversible, the rate of desorption being equal to the rate of exchange. They propose the existence of two forms of bond between chemisorbed oxygen and a silver surface. Increasing the amount of strongly bound oxygen lowers the rate of desorption, but does not affect the activation energy for desorption (32.5 kcal mole^{-1}). Fast diffusion and exchange occur over the whole of the surface, but only the oxygen less firmly bound to the surface is desorbed.

IV. RELATIONSHIP BETWEEN THE CATALYTIC ACTIVITY OF OXIDES TOWARDS OXYGEN EXCHANGE AND THEIR ACTIVITY TOWARDS OTHER OXIDATION REACTIONS

In the previous Sections we have shown that the catalytic activity of oxides and of oxygen-saturated metals towards the isotopic exchange of molecular oxygen is essentially determined by the energy of the bond between oxygen and the surface layer of the catalyst. It is natural to suppose that the oxygen bond energy may also be the key factor in other oxidation reactions taking place on these catalysts with the participation of oxygen.

It is interesting, therefore, to examine the catalytic activity of oxides towards these processes. The data chosen to be discussed here were confined to oxides with an equilibrium oxygen content. Accordingly, we select, for comparison, data on oxidation reactions taking place in an oxidising medium (i.e. with an excess of oxygen in the reaction mixture). It would have been very interesting to establish to what extent oxides with a non-equilibrium oxygen content, which show low-temperature activity towards oxygen exchange, can accelerate other oxidation reactions, but the available experimental material is insufficient for this purpose.

1. Catalytic Oxidation of Hydrogen

This reaction was studied by Popovskii and Boreskov [59] on the actual oxide samples used [8] to investigate isotopic exchange in molecular oxygen. The experiments were made by a stationary–circulation method [60], which allowed the reaction rate to be measured directly in the presence of a large excess of oxygen. The data for manganese dioxide are taken from the work of Bruns [61]. Complete consistency was found between the activity of transition metal oxides of the fourth period towards homomolecular oxygen exchange and towards the oxidation of hydrogen (curves *1* and *2* of Fig. 11). Consistency between changes in catalytic activity towards oxygen exchange and towards the oxidation of hydrogen is found also for vanadium catalysts promoted by alkali metal sulphates [48].

2. Oxidation of Carbon Monoxide

The very extensive literature on the activity of various oxides towards the oxidation of CO was reviewed by Krylov [62]. A statistical treatment was applied in an attempt to allow for the reliability of the various data by appropriate weighting factors. The relative activities of the oxides of the fourth period were found to be

MnO_2	Co_3O_4	NiO	CuO	ZnO	TiO_2	Fe_2O_3	V_2O_5	Cr_2O_3
310	200	100	83	22	18	16	11	11

This activity sequence with respect to the oxidation of CO is very close to the sequence found for the oxygen isotope exchange.

Stone [63] arrived at the following sequence of catalytic activities for the oxides by analysing published data on the oxidation of CO

$$CoO > NiO > MnO_2 \text{ from } 0° \text{ to } 150°C$$
$$CuO > Fe_2O_3 > ZnO > TiO_2 > Cr_2O_3 > V_2O_5 \text{ from } 150° \text{ to } 400°C$$

Again, the oxides of cobalt, nickel, manganese, and copper are the most active.

3. Complete Oxidation of Hydrocarbons

The results of a study of the activity of various catalysts towards the oxidation of methane in a flow–circulation apparatus are shown as curve *3* of Fig. 11. The change in specific catalytic activity for the series of fourth period oxides is similar to the change observed in the homomolecular exchange of oxygen. The same conclusion is reached if the comparison is made with the results of Gerald and

Horvatisch[65], who established the following activity sequence for the various catalysts

$$Co_3O_4 > MnO_2 > Pt > NiO > CuO > Cr_2O_3 > Fe_2O_3 > ZnO .$$

Stein and coworkers[66] made a systematic study of the activity of a large number of oxides towards the complete oxidation of hydrocarbons with five and six carbon atoms. The most active was Co_3O_4; a high activity was noted in most cases with manganese and nickel oxides; the lowest activity was shown by zinc oxide and vanadium pentoxide.

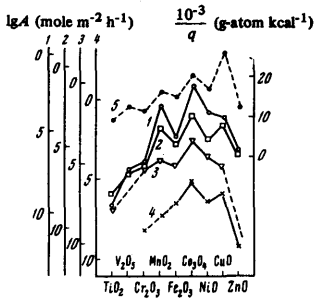


Figure 11. Specific catalytic activity of the oxides of metals from the fourth period towards oxidation reactions:
1) homomolecular oxygen isotope exchange; *2*) oxidation of hydrogen; *3*) oxidation of methane; *4*) decomposition of nitric oxide; *5*) reciprocal heats of formation of the oxides referred to 1 g-atom of oxygen.

Minachev and coworkers[67] studied the activity of the rare-earth oxides towards the complete oxidation of propene. They point out that the activity of these oxides appears in the temperature range corresponding to appreciable mobility of the surface oxygen[41]. A comparison of the extent of conversion of propene to CO_2 and of the rate of exchange of O_2 with the oxygen of the rare-earth oxides reveals a definite correspondence between these characteristics. The change in activity as a function of the atomic number of the element corresponds to the classification of these oxides into the cerium and the yttrium subgroups, both for oxygen exchange and for the oxidation of propene.

4. Oxidation of Ammonia

Kurin and Zakharov[68] found that the activity of the oxides of fourth period metals towards the high-pressure oxidation of ammonia decreases in the following order:

$$Co_3O_4 > MnO_2 > Cr_2O_3 > CuO > NiO > Fe_2O_3 > ZnO > TiO_2 .$$

Except for the position of chromium oxide, this series is very similar to the corresponding series for the isotope exchange reaction in oxygen.

5. Decomposition of Nitric Oxide

Curve *4* of Fig. 11 shows the relative catalytic activities of the oxides of the elements of the fourth period towards the decomposition of NO, measured in a static circulation apparatus[69]. MnO_2 and CuO were found to be unstable under the conditions of the reaction. The activity of the other oxides varies in the same sense as their activity towards homomolecular oxygen exchange.

6. Oxidation of Sulphur Dioxide

The activities of the various oxides towards this reaction cannot be compared, because most of them are converted into inactive sulphates under the conditions of the reaction. The only exception is vanadium pentoxide, whose activity is significantly increased by promotion with alkali metal sulphates.

As Fig. 7 shows, the catalytic activity of vanadium catalysts containing alkali metal sulphates varies in the same sense for isotope exchange in molecular oxygen and for the oxidation of sulphur dioxide.

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In spite of occasional discrepancies, not surprising in view of differences in sample preparation, purity, and experimental conditions, the examples considered undoubtedly show that the activity of oxides towards exchange in molecular oxygen is characteristic also of their activity towards various other oxidation reactions. In many cases, as for example in the oxidation of hydrogen, the correlation between the specific catalytic activities towards oxygen exchange and towards the oxidation reaction on the various catalysts is so striking that a common rate-limiting step for the two reactions can be postulated. For the hydrogen oxidation and the molecular oxygen exchange reactions this limiting step could be the chemisorption of oxygen. However, the activation energy and the kinetic order with respect to oxygen[9,59,70] of the oxygen exchange and the hydrogen oxidation reactions are quite different. Hence we must reject the hypothesis of a common rate-limiting step. The only possible conclusion is that although the rate-limiting steps of the two reactions are different, the catalytic activity depends on one and the same property of the oxides, which varies along the series of catalysts considered. It is natural to suppose that this property must be the bond energy between the oxygen and the surface layer of the oxide. In isotope exchange reactions this quantity determines the activation energy for adsorption and desorption of oxygen, and in the oxidation of hydrogen it determines the activation energy for the interaction of hydrogen with the oxygen on the oxide surface. In a similar way, the activation energy for the interaction of the reducing agent with the oxygen on the surface of the oxide can be determined as for other oxidation reactions by the binding energy of the oxygen on the surface layer of the oxide.

Thus, the binding energy of the oxygen is one of the basic factors controlling the activity of oxides towards oxidation reactions. However, the rate of isotope exchange in molecular oxygen, readily measured experimentally, can be a convenient quantitative criterion of the reactivity of the oxygen on the surface of an oxide.

Nevertheless, the prediction of the catalytic efficiency for oxidation reactions remains a complicated problem, since the simple dependence on the reactivity of the surface oxygen may be masked by the influence of numerous other factors. Thus, the catalytic activity may be limited by the stability of the oxide phase under the conditions of the catalytic reaction: an example of this behaviour is the oxidation of SO_2, discussed above, in which the activity of most oxides is extremely low because of their conversion into sulphates. If the Co_3O_4 phase had been more stable than cobalt sulphate under the conditions of the reactions,

cobalt catalysts would probably have been much more active than vanadium catalysts towards the oxidation of SO_2.

A complicated dependence on the reactivity of the surface oxygen can be expected also for partial oxidation reactions, in which the yield of the desired product is determined by the relative rates of a number of competitive and consecutive reactions.

In some cases the interaction between the material to be oxidised and the catalyst (chemisorption) can be the limiting step, instead of the subsequent reaction with the oxygen on the catalyst surface. The possibility that some oxidation reactions may proceed by interaction between the reducing agent and molecular oxygen cannot be excluded. This possibility has been examined in detail by Margolis[71]. In the latter two cases the correlation with the reactivity of the oxygen on the oxide surface may be very weak or altogether absent.

Lastly, even if the interaction with the oxygen on the oxide surface is the rate-limiting step, the simple correlation with the reactivity may be obscured by the decrease in the concentration of surface oxygen brought about by the reaction itself: this effect can have a profound influence on the properties of the surface oxygen. To a greater or lesser extent, this complication can be expected in all cases. It may be avoided, however, by measuring the reactivity of the oxygen on the oxide surface during the actual oxidation reaction.

In spite of the many complicating factors listed above, the bond energy of the oxygen in the surface layer of the oxide can be used as the basis for a generalisation of the experimental data and for the choice of catalysts for reactions involving the transfer of oxygen atoms between reactant molecules.

V. PARTICIPATION OF OXYGEN FROM OXIDE CATALYSTS IN OXIDATION REACTIONS

Transition metal oxides have found wide applications as the active components of oxidation catalysts. To explain the mechanism of oxidation reactions, involving the transfer of oxygen between molecules of the reacting materials, it is important to establish whether the oxygen of the catalyst plays a direct part in these transfers.

One possible assumption is that the oxygen to be added to the reducing component is taken from the surface layer of the crystal lattice of the catalyst, the oxygen loss in this layer being continuously replenished by the second component (capable of giving up oxygen). It must be stressed that these elementary processes of oxygen loss and oxygen addition involve no phase changes in the catalyst.

A second variant of the mechanism is based on the assumption that the transfer of oxygen from the oxidising to the reducing component takes place without intermediate conversion of the oxygen into an anion on the surface layer of the catalyst lattice. The energy and nature of the intermediate formed between the oxygen and the catalyst in this case are quite different from those of the oxygen bond in the oxide.

When comparing these variants, we should not try to reach a general conclusion. The correctness of one or other of the above assumptions depends on the nature of the catalyst, the nature of the reactants, and the conditions of the reaction. The discussion given in this review of the simplest oxidation reaction—isotope exchange in molecular oxygen—provides a good illustration of the state of affairs. With oxides which have been treated in oxygen at high temperatures, and whose surface layer therefore has acquired the equilibrium composition for the particular oxygen pressure, the rate of exchange in molecular oxygen is always the same as the rate of isotope exchange with the oxygen of the catalyst surface. This is evidence that the first of the above variants of the mechanism applies to this reaction. The form of the intermediate in the reaction between oxygen and the catalyst coincides, in this case, with the form of the oxygen bond in the surface layer of the oxide (or is so close to it that fast transitions between them are possible). The existence of other forms of atomically bound oxygen is unlikely under these conditions, and in any case the rate of formation of such structures should be considerably lower than the rate of binding of the oxygen in the surface layer of the oxide, since the exchange of molecular oxygen would otherwise take place through this form and its rate would be higher than the rate of exchange with oxygen.

On the other hand, oxides with a non-equilibrium oxygen content in the surface layer, prepared by a special heat treatment and active towards exchange at relatively low temperatures, give a rate of exchange in molecular oxygen considerably in excess of the rate of exchange with the oxygen of the oxide. This proves beyond doubt the correctness of the second variant of the mechanism.

These results can be of use also in identifying the mechanism of more complex oxidation reactions. The rate of exchange of molecular oxygen is characteristic of the rate of binding of oxygen by the catalyst. If the oxidation reaction takes place through the same intermediate form, produced by the interaction of oxygen with the catalyst, this step will be common to the two reactions. Simple comparison of the rates is not sufficient, however, to identify the mechanism of the oxidation reaction.

Because of the reaction with the component to be oxidised, the concentration of oxygen in the surface layer of the oxide under the conditions of the oxidation reaction may be lower—and the rate of binding of oxygen may therefore be significantly higher—than under conditions of exchange of molecular oxygen on oxides with an equilibrium oxygen content. Therefore, a rate of oxidation higher than the rate of exchange for the same temperature and oxygen pressure does not preclude oxidation through interaction with the oxygen of the oxide. Direct measurements of the rate of transfer of oxygen from the oxide to the reaction products are needed. These measurements are possible in principle (by introducing the heavy oxygen isotope into the oxide composition), but unambiguous conclusions are not always possible because of complicating factors.

Most of the work has been on the oxidation of carbon monoxide on manganese dioxide, copper oxide, and some other oxides. The first investigations[72,73] led to the conclusion that the oxygen of the oxide catalysts takes part in the reaction. On the other hand, Vainshtein and Turovskii[74,75] failed to observe a significant change in the isotopic composition of the catalyst after oxidising CO on MnO_2 and CuO enriched with ^{18}O. The sensitivity of the method would have allowed ~ 5% exchange of the oxygen of the catalyst to be detected, corresponding to several monolayers. The authors suggested, on the evidence of stepwise oxidation experiments on reduced oxides by successive additions of oxygen of different isotopic composition, that the mobility of oxygen in their oxides was high enough to ensure a uniform isotopic composition in the bulk and on the surface under the conditions of the experiment. However, direct measurements of the mobility of oxygen in MnO_2 [43] and CuO [42] have shown that the oxygen has no significant mobility in these oxides under the conditions of the CO oxidation experiments. Therefore, the work of Vainshtein and Turovskii, which showed that oxygen from the

bulk of the oxides does not take part in the oxidation of CO on MnO_2 and CuO, leaves unresolved the question of whether the oxygen on the surface of the catalyst (and, more to the point, the most active part of this oxygen) takes part in the reaction.

Winter[76] studied the mechanism of the oxidation of CO on NiO and Cr_2O_3 and concluded that only a small fraction (no more than 2.5%) of the surface oxygen of the catalyst was involved. With Cu_2O, however, between 10 and 40% of the surface oxygen took part in the reaction, the fraction increasing at higher reaction temperatures.

Popovskii and coworkers[77], in their work on the participation of oxygen from the surface of Co_3O_4 in the oxidation of hydrogen at 75°C, found that between 2 and 20% reacted if the sample had been activated at 400°C, whereas between 13 and 39% of the surface oxygen reacted on a sample which had been merely evacuated at 75°C. The low precision of these measurements is due to the need to apply corrections for the exchange of oxygen isotopes between the catalyst and the water vapour formed by the reaction.

Roiter and coworkers studied the participation in oxidation reactions of the oxygen of vanadium pentoxide with the help of ^{18}O. In the oxidation of naphthalene[78] on ^{18}O-enriched vanadium pentoxide the concentration of this isotope in the catalyst did not decrease within the limits of the measurement accuracy (~ 10%). If the whole of the oxygen used in the oxidation of naphthalene had been taken from the surface of the vanadium pentoxide, with complete mixing of the oxygen within the catalyst, the final concentration of ^{18}O in the vanadium pentoxide should have been 10–30% lower than the initial concentration. The authors concluded that the oxygen of vanadium pentoxide does not take part in the oxidation of naphthalene. This conclusion cannot be accepted unreservedly in view of the low mobility of oxygen within vanadium pentoxide crystals, inferred from the large departure from first order of the exchange kinetics in water vapour[40] at these temperatures (340–390°C).

In the oxidation of sulphur dioxide on ^{18}O-enriched vanadium pentoxide[79] the concentration of this isotope was found to decrease, but by no more than after oxygen exchange under the same conditions. If oxygen from the V_2O_5 surface had been involved in the oxidation of SO_2, the loss of ^{18}O from the catalyst should have been accelerated by the reaction. At the higher experimental temperatures of this work (500–610°C) inadequate mobility of the oxygen from the catalyst ceases to be an obstacle. The result of Kasatkina and Shustov[80] do not support these conclusions: these workers showed that SO_3 exchanges with the oxygen of vanadium pentoxide at a rate well in excess of the rate of oxidation of sulphur dioxide. This observation adds further complexity to the problem of the participation of oxygen from the oxide in the reaction.

Roiter and Yuza[70] made separate measurements of the rates of reduction of vanadium pentoxide by hydrogen and of oxidation by oxygen, and by comparing the results with the rate of the catalytic oxidation of hydrogen on V_2O_5 they concluded that the oxygen of vanadium pentoxide does not enter into the catalytic reaction.

All these researches enable us to conclude with some confidence that oxygen from the bulk of the oxides does not take part in catalytic oxidation reactions. This conclusion is in keeping with the general proposition that reactions involving a phase transformation cannot be invoked as stages of a catalytic process. The problem of whether oxygen from the surface of the oxides is involved in catalytic oxidation is more difficult to resolve. For the oxidation of CO and H_2 on NiO, CuO, and Co_3O_4 we believe that the bulk of the evidence points to participation of some—the most active part—of the oxygen on the oxide surface. This conclusion is supported not only by direct experimental data but also by the similarity between the relative activities of the various oxides towards these reactions on the one hand and towards exchange in molecular oxygen on the other hand. For the latter reaction it has been established that oxygen from the surface of the oxides is involved, and that oxygen sorption on the surface of these oxides cannot occur at significant rates to give an atomic form, which has bonding substantially different from the oxygen bond in the surface layer of the crystal lattice of the oxide. The last conclusion follows from the equality of the rates of exchange in molecular oxygen and of isotope exchange with the oxygen of the oxide.

It is possible, however, that at lower temperatures and when the surface layer of the oxide shows large departures from its equilibrium oxygen composition, the oxidation will occur through some other form of chemisorbed oxygen, as is the case in the exchange of molecular oxygen on specially activated oxides.

Data on the catalytic oxidation reactions on vanadium pentoxide are still too scanty for unambiguous conclusions. It is possible that the rate of sorption of oxygen and the form of the oxygen bond to the catalyst are substantially altered by the simultaneous adsorption of the compound to be oxidised. This argument, put forward by Roiter[81], is particularly relevant when the adsorption of oxygen and of the oxidisable species is accompanied by electron transfers in opposite directions. There is experimental evidence of a positive effect on the rate of adsorption by preliminary adsorption of another material[82,83].

An extension of the study of the participation of oxygen from the oxides in oxidation reactions, to include a wider range of oxide catalysts and of reactions, would undoubtedly be of interest.

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Studies of the catalysis of isotope exchange in molecular oxygen began relatively recently, and have so far been confined to a limited number of catalysts and a relatively narrow range of reaction conditions. Nonetheless, the results obtained justify the hope that this reaction will prove to be a useful method of studying the mechanism of oxidation reactions, and particularly convenient for characterising the intermediate forms in the interaction between oxygen and solid catalysts.

The most important result obtained so far is the conclusion that exchange in molecular oxygen on the one hand, and isotope exchange with the oxygen of the catalyst (in the case of oxides with an equilibrium oxygen concentration in the surface layer) on the other hand, proceed at equal rates. This equality of rates points to the participation of oxygen from the catalyst in exchange reactions, and also suggests that the oxygen chemisorbed by oxides has the same (or nearly the same) bond energy as the oxygen of the surface layer of the oxide crystal lattice. Hence, the rate of exchange of molecular oxygen can serve as a general characteristic of the reactivity of the oxygen, and can be a useful guide to the rules for the choice of catalysts for oxidation reactions.

The surface oxygen of catalytically active oxides is non-uniform, the degree of non-uniformity being greater, the more active the oxide. There is no simple relationship between the catalytic activity towards exchange and the electronic work function of oxides.

Under the conditions leading to isotope exchange on metals (Pt, Pd, Ag), considerable sorption of oxygen in the surface layer of the metal (equivalent to several monolayers) is observed. In this form, the metals behave very much like oxides towards the catalysis of exchange in molecular oxygen. Platinum is very similar to the most active oxide (Co_3O_4) in the values of the activation energy and of the absolute rate of exchange, and in the nature of the non-uniformity.

The high catalytic activity towards oxygen exchange at low temperatures shown by oxides which have been subjected to strong activation in a vacuum is extremely interesting. The low-temperature activity is short-lived, particularly at high temperatures, and is evidently caused by the departure from equilibrium composition of the oxide brought about by the activation. Isotope exchange with the oxygen of the oxide does not occur under these conditions. Homomolecular exchange on oxides activated in this way involves special intermediate forms of interaction between the oxygen and the catalyst. Studies of the possible role of these forms in the catalysis of oxidation reactions are highly desirable.

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The Electron Spin Resonance Method in Photochemistry

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The electron spin resonance (ESR) method is, at the moment, one of the most sensitive physical methods of detecting, identifying, and studying free radicals, ion-radicals, and molecules in the triplet state formed during photochemical reactions. In this review, the use of the ESR method in studies of photodecomposition and photoionisation reactions of simple and of complex compounds is discussed on the basis of results obtained by Soviet and foreign workers. It is concluded that the ESR method will prove to be a powerful physical method of investigation of photochemical systems only if used in conjunction with other methods (in particular, optical spectroscopy).

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I. INTRODUCTION

For many years, chemical analysis of the final reaction products has been the most widely used method of investigating the mechanism of photochemical reactions. Knowing the products, one can surmise the nature of the intermediate stages. Methods of separation and of analysis of the reaction products have reached an advanced level of development. For the identification of products, chemists can call on methods such as chromatography, mass spectroscopic analysis, and tracer methods. It is well known that excited states, ions, and free radicals play a key role in photochemical change. If the optical absorption or luminescence spectra of these intermediate states are known, direct identification using the ultraviolet, visible, or infrared bands is possible in principle. However, this approach is often precluded by the extremely short lifetimes of photochemical reaction intermediates.