

## Exchange Reactions of Oxygen between Oxygen Molecules and Solid Oxides

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Received August 8, 1963

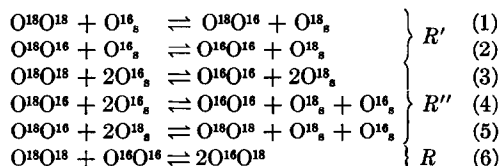
A theory is presented which describes the isotope exchange reactions occurring in the system containing oxygen molecules and an oxide. This theory has been tested by the time dependences of the concentrations of  $O^{18}O^{18}$ ,  $O^{18}O^{16}$ , and  $O^{16}O^{16}$  molecules over magnesium oxide.

Considerable attention has been paid to the exchange reactions between gaseous oxygen and solid oxides, in which the rates of the changes both in the concentration of atomic-labeled oxygen (1) and in the concentration of individual molecules (2)  $O^{18}O^{18}$ ,  $O^{16}O^{16}$ , and  $O^{16}O^{18}$  have been followed. We wish to present a complete kinetic treatment of this system and demonstrate its usefulness in comparison with experimental data.

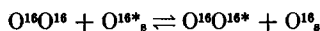
### THEORY

#### *Formulation of the Problem*

The exchange reactions of  $O^{18}$  and  $O^{16}$  which can take place in a system containing gaseous oxygen and a solid oxide, the amount of intermediate particles being negligibly small, are described by the following scheme.



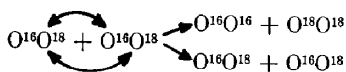
In this scheme are not included such reactions in which the exchange occurs but does not lead to a change in isotopic composition, e.g.



(probability  $p_2$ , see below, is equal to zero). The index  $s$  denotes oxygen atoms of the solid oxide.

There are three possible ways in which the gaseous molecule can exchange its oxygen in the presence of a solid oxide. Either the molecule exchanges one of its oxygen atoms with the solid oxide, or two atoms with the oxide, or exchanges one of its atoms with another oxygen molecule; it is irrelevant for the kinetic treatment whether the last process is catalyzed by the surface of the oxide or other surfaces in the apparatus or whether it takes place in the gas phase. In the following we will denote by  $R'$  the number of elementary acts of exchange per unit time, in which one molecule exchanges one oxygen atom with the oxide; by  $R''$ , the number of acts per unit time in which one molecule exchanges two atoms with the oxide; and by  $R$ , the number of molecules per unit time exchanging their atom with another oxygen molecule. Then the rate of change in number of molecules of a given isotopic composition in a chosen reaction [one of the reactions (1) - (6) from the right or left] is given by the expression  $(1/n) \times K \times p_1 \times p_2$ , where  $K$  is  $R$ ,  $R'$ , and  $R''$ , respectively, and  $p_1$  is the probability of simultaneous presence of molecules and atoms of the given isotopic composition in the chosen reaction. The quantity  $n$  is the number of molecules converted in the chosen reaction per one molecule of the isotopic species whose conversion is followed; e.g. in reaction (6), when the conversion of  $O^{18}O^{18}$  is followed,  $n$  is equal to 2, because two molecules of oxygen ( $O^{18}O^{18}$  and  $O^{16}O^{16}$ ) are

converted per molecule of  $O^{18}O^{18}$ . The factor  $1/n$  normalizes the reaction rate  $K$  so that it is always related to the same number of molecules whose conversion is followed; e.g. in reaction (6) only one-half of the molecules exchanging their oxygen are the molecules  $O^{18}O^{18}$ . The quantity  $p_2$  is the probability that when exchange occurs between molecules and/or atoms of the given isotopic composition in the chosen reaction, it will also lead to the change in number of molecules of the isotopic composition followed. For example, in reaction (6) from the right to the left, the exchange can take place in two ways:



both of them being equally likely, but only the first one leading to the change in isotopic composition of the molecules;  $p_2$  is thus equal to  $\frac{1}{2}$ .

If it is assumed that (1) different isotopes undergo reactions at the same rate (neglecting the isotopic effect), (2) transport phenomena are considerably faster than the exchange reactions, and (3) all exchangeable oxygen atoms of the solid oxide are equivalent, the kinetics in reactions (1) – (6) can be formulated as follows. [The criterion of fulfillment of these assumptions is experimental verification of Eq. (12) below.]

Let  $x$ ,  $y$ ,  $z$ , be numbers of molecules  $O^{18}O^{18}$ ,  $O^{16}O^{18}$ , and  $O^{16}O^{16}$ , respectively;  $w$ , the number of  $O^{18}$  atoms in the gaseous phase,  $u$ , the number of  $O^{18}$  exchangeable atoms in the solid oxide;  $v$ , the number of exchangeable  $O^{16}$  atoms in the solid oxide;  $c$ , the total number of exchangeable  $O^{18}$  atoms in the system;  $m$ , the total number of exchangeable oxygen atoms in the solid; and  $a$ , the total number of oxygen molecules in the gaseous phase. Then the rates of the change in number of  $O^{18}O^{18}$  molecules with time in each reaction (1) – (6) in either direction (direction is indicated by an arrow) are given by the following expressions.

$$\begin{array}{ll}
 -\left(\frac{dx}{dt}\right)_{(1)}^{\rightarrow} = R' \frac{xv}{am} & n = 1, p_1 = \frac{x}{a} \times \frac{v}{m}, p_2 = 1 \\
 -\left(\frac{dx}{dt}\right)_{(1)}^{\leftarrow} = -\frac{1}{2} R' \frac{yu}{am} & n = 1, p_1 = \frac{y}{a} \times \frac{u}{m}, p_2 = \frac{1}{2} \\
 -\left(\frac{dx}{dt}\right)_{(3)}^{\rightarrow} = R'' \frac{xv(v-1)}{am(m-1)} & n = 1, p_1 = \frac{x}{a} \times \frac{v}{m} \times \frac{(v-1)}{(m-1)}, p_2 = 1 \\
 -\left(\frac{dx}{dt}\right)_{(3)}^{\leftarrow} = -R'' \frac{zu(u-1)}{am(m-1)} & n = 1, p_1 = \frac{z}{a} \times \frac{u}{m} \times \frac{(u-1)}{(m-1)}, p_2 = 1 \\
 -\left(\frac{dx}{dt}\right)_{(5)}^{\leftarrow} = R'' \frac{2xw}{am(m-1)} & n = 1, p_1 = \frac{x}{a} \times 2 \times \frac{u}{m} \times \frac{v}{(m-1)}, p_2 = 1 \\
 -\left(\frac{dx}{dt}\right)_{(5)}^{\rightarrow} = -R'' \frac{yu(u-1)}{am(m-1)} & n = 1, p_1 = \frac{y}{a} \times \frac{u}{m} \times \frac{(u-1)}{(m-1)}, p_2 = 1 \\
 -\left(\frac{dx}{dt}\right)_{(6)}^{\rightarrow} = \frac{1}{2} R \frac{2xz}{a(a-1)} & n = 2, p_1 = 2 \times \frac{x}{a} \times \frac{z}{(a-1)}, p_2 = 1 \\
 -\left(\frac{dx}{dt}\right)_{(6)}^{\leftarrow} = -\frac{1}{4} R \frac{y(y-1)}{a(a-1)} & n = 2, p_1 = \frac{y}{a} \times \frac{(y-1)}{(a-1)}, p_2 = \frac{1}{2}
 \end{array}$$

If it is taken into account that  $a, x, y, z, u, v, m \gg 1$ , the total change in number of  $O^{18}O^{18}$  molecules with time is given by

$$-\frac{dx}{dt} = R' \left( \frac{xv}{am} - \frac{1}{2} \frac{yu}{am} \right) + R'' \left( \frac{xv^2}{am^2} - \frac{zu^2}{am^2} + 2 \frac{xwv}{am^2} - \frac{yu^2}{am^2} \right) + \frac{R}{2} \left( 2 \frac{xz}{a^2} - \frac{1}{2} \frac{y^2}{a^2} \right) \quad (7)$$

Since it holds that

$$\begin{aligned} x + y + z &= a \\ 2x + y &= w \\ v + u &= m \\ w + u &= c, \end{aligned}$$

Eq. (7) can be rewritten as

$$-\frac{dx}{dt} = \frac{R}{a} \left[ x - \frac{1}{a} \left( \frac{w}{2} \right)^2 \right] + \frac{R'}{a} \left[ x - \frac{w(c-w)}{2m} \right] + \frac{R''}{a} \left[ x - \frac{a}{m^2} (c-w)^2 \right] \quad (8)$$

Similarly for  $dy/dt$  it holds that

$$\begin{aligned} \frac{dy}{dt} = R \left( \frac{2xz}{a^2} - \frac{y^2}{2a^2} \right) + R' \left( \frac{xv}{am} - \frac{yu}{2am} - \frac{yv}{2am} + \frac{zu}{am} \right) \\ + R'' \left( -\frac{yv^2}{am^2} + \frac{2zuv}{am^2} - \frac{yu^2}{am^2} + \frac{2xuv}{am^2} \right) \quad (9) \end{aligned}$$

or

$$\begin{aligned} \frac{dy}{dt} = \frac{2R}{a} \left[ x - \frac{1}{a} \left( \frac{w}{2} \right)^2 \right] + \frac{R'}{a} \left[ -y + w \left( \frac{1}{2} - \frac{a}{m} - \frac{c}{m} \right) + \frac{w^2}{m} + \frac{ac}{m} \right] \\ + \frac{R''}{a} \left[ -y + \frac{2a}{m^2} (c-w)(m-c+w) \right]. \quad (10) \end{aligned}$$

*Solution*

Since the total number of oxygen atoms in the gas and in the solid, as well as the total number of  $O^{18}$  atoms in the system, do not change with time, the quantities  $a, m, c, R, R',$  and  $R''$  are time-independent constants and the above system of equations can be solved in the following manner.

By substituting from (8) and (10) into

$$\frac{dw}{dt} = 2 \frac{dx}{dt} + \frac{dy}{dt}$$

we obtain

$$\frac{dw}{dt} = -(2R'' + R') \left( \frac{2a+m}{2am} \right) \left( w - \frac{2ac}{2a+m} \right) \quad (11)$$

which gives after integration from  $t = 0$  to  $t$

$$w = \frac{2ac}{2a+m} + \left( w_0 - \frac{2ac}{2a+m} \right) \exp \left[ -(2R'' + R') \left( \frac{2a+m}{2am} \right) t \right]$$

or

$$w - w_\infty = (w_0 - w_\infty) \exp \left[ -(2R'' + R') \left( \frac{2a+m}{2am} \right) t \right], \quad (12)$$

where  $w_0$  is the value of  $w$  at  $t = 0$ , and  $w_\infty = 2ac/(2a+m)$  represents the value of  $w$  at  $t = \infty$ .

The number of  $O^{18}$  atoms in the gaseous phase,  $w$ , thus changes according to the equation of first order (12).

If we now substitute for  $w$  from (12) into (8) and integrate in limits  $t = 0$  and  $t$ , we obtain

$$\begin{aligned}
 x = & \frac{ac^2}{(2a+m)^2} + (w_0 - w_\infty) \left( \frac{c}{2a+m} \right) \exp \left[ -(2R'' + R') \left( \frac{2a+m}{2am} \right) t \right] \\
 & - \left\{ \frac{1}{2m} (w_0 - w_\infty)^2 \frac{[1 + (m^2R/4a^2R'') - (mR'/2aR'')] }{[2 + (m/2a) - (mR/2aR'') + (R'/R'')] } \right. \\
 & \quad \left. \times \exp \left[ -(2R'' + R') \left( \frac{2a+m}{am} \right) t \right] \right\} \\
 & + \left\{ x_0 - \frac{ac^2}{(2a+m)^2} - (w_0 - w_\infty) \left( \frac{c}{2a+m} \right) + \frac{1}{2m} (w_0 - w_\infty)^2 \right. \\
 & \quad \left. \times \frac{[1 + (m^2R/4a^2R'') - (mR'/2aR'')] }{[2 + (m/2a) - (mR/2aR'') + (R'/R'')] } \right\} \times \exp \left[ -\frac{1}{a} (R + R' + R'')t \right]. \quad (13)
 \end{aligned}$$

Here  $x_0$  is the value of  $x$  at  $t = 0$ .

Equation (13) describes the dependence of the number of  $O^{18}O^{18}$  molecules on time. Similarly for  $y$  one obtains

$$\begin{aligned}
 y = & \frac{2ac(2a+m-c)}{(2a+m)^2} + (w_0 - w_\infty) \left( \frac{2a+m-2c}{2a+m} \right) \exp \left[ -(2R'' + R') \left( \frac{2a+m}{2am} \right) t \right] \\
 & + \left\{ \frac{1}{m} (w_0 - w_\infty)^2 \frac{[1 + (m^2R/4a^2R'') - (mR'/2aR'')] }{[2 + (m/2a) - (mR/2aR'') + (R'/R'')] } \right. \\
 & \quad \left. \times \exp \left[ -(2R'' + R') \left( \frac{2a+m}{am} \right) t \right] \right\} \\
 & + \left\{ y_0 - \frac{2ac(2a+m-c)}{(2a+m)^2} - (w_0 - w_\infty) \left( \frac{2a+m-2c}{2a+m} \right) \right. \\
 & \quad \left. - \frac{1}{m} (w_0 - w_\infty)^2 \frac{[1 + (m^2R/4a^2R'') - (mR'/2aR'')] }{[2 + (m/2a) - (mR/2aR'') + (R'/R'')] } \right\} \exp \left[ -\frac{1}{a} (R + R' + R'')t \right] \quad (14)
 \end{aligned}$$

Equation (14) describes the dependence of the number of  $O^{16}O^{18}$  molecules on time,  $y_0$  being the initial amount of  $O^{16}O^{18}$  molecules in the system.

#### The Quantity $y^2/xz$

The quantity  $y^2/xz$  is an important characteristic of the system under consideration since it is a measure of deviation from equilibrium during the exchange. It can easily be shown that at time  $t = \infty$ ,  $y_\infty^2/x_\infty z_\infty = 4$ ; this is the magnitude of equilibrium constant for the exchange in gaseous oxygen which must be attained at the end of reaction.

We shall now consider a special case when also the initial concentrations satisfy the relation  $y_0^2/x_0 z_0 = 4$ . If  $R'' = 0$ , then  $y^2/xz = 4$  during the whole reaction (Fig. 3, curve 1). If  $R'' \neq 0$  and  $R' = R = 0$ , the time dependence of  $y^2/xz$  exhibits a minimum as demonstrated, e.g., in Fig. 3, curve 2.

Any other case, i.e.

$$\begin{aligned}
 R'' \neq 0, R' \neq 0, R = 0 \\
 R'' \neq 0, R' = 0, R \neq 0 \\
 R'' \neq 0, R' \neq 0, R \neq 0
 \end{aligned}$$

falls between the two above mentioned limiting cases.

#### Procedure in Experimental Determination of $R$ , $R'$ , and $R''$

Evidently, all three constants  $R$ ,  $R'$ , and  $R''$  may be obtained from one experiment in which the time dependences of  $x$  and  $y$  are followed. First,  $m$  is determined from the meas-

ured value of  $w_\infty = 2ac/(2a + m)$  and the known values of  $a$  and  $c$ . The sum  $\alpha = 2R'' + R'$  is then determined from the slope of  $\log(w - w_\infty)/(w_0 - w_\infty)$  vs.  $t$  plot according to Eq. (12). Subsequently, the constants  $R$ ,  $R'$ , and  $R''$  are varied in such a way that the value of  $\alpha$  is preserved and at the same time best fit is obtained of the theoretical dependence (13) or (14), respectively, to the experimental dependence of  $x$  on  $t$  or  $y$  on  $t$ , respectively. It is possible to program this procedure for an automatic computer.

However, sometimes the following method may prove advantageous. Two experiments are performed in the same oxygen-oxide system: experiment I, in which  $w_0 \neq w_\infty$ , and experiment II, in which the isotopic composition of the gaseous mixture is such that  $w_0 = w_\infty$  but  $x_0 \neq x_\infty$  and  $y_0 \neq y_\infty$ . The conditions of experiment II are realized when a nonequilibrium gaseous mixture is subjected to the exchange reaction in which atomic  $O^{18}$  has the same concentration in the gaseous phase and in the solid,  $w_0/2a = u_0/m$ . Since, for experiment II,  $w_0 - w_\infty = 0$ , Eq. (13) reduces to

$$x = x_\infty + (x_0 - x_\infty) \exp[-(1/a)(R + R' + R'')t] \quad (15)$$

and Eq. (14) to

$$y = y_\infty + (y_0 - y_\infty) \exp[-(1/a)(R + R' + R'')t] \quad (16)$$

where

$$x_\infty = \frac{ac^2}{(2a + m)^2} \quad \text{and} \quad y_\infty = \frac{2ac(2a + m - c)}{(2a + m)^2}$$

Since in experiment II  $dw/dt = 0$ , there is no transfer of  $O^{18}$  from gas to the solid and vice versa and the only reaction which apparently takes place is the equilibration of gaseous mixture. Equations (15) and (16) show that this equilibration proceeds, under the conditions of experiment II, as a reaction of first order. The sum  $\beta = R + R' + R''$  can be determined from the slope of  $\log(x - x_\infty)/(x_0 - x_\infty)$  vs.  $t$  plot. Now  $\alpha$  and  $\beta$  are inserted into Eq. (13), using the values of  $w_0$  and  $x_0$  for experiment I, and the ratio

$$\gamma = \frac{[1 + (m^2R/4a^2R'') - (mR'/2aR'')]}{[2 + (m/2a) - (mR/2aR'') + (R'/R'')]} \quad (17)$$

is varied until the best fit of the theoretical  $x$  vs.  $t$  curve to the experimental points is obtained. From  $\alpha$ ,  $\beta$ , and the best values of  $\gamma$  one can compute all three constants  $R$ ,  $R'$ , and  $R''$ .

The latter method has the advantage that only one parameter,  $\gamma$ , is varied.

#### EXPERIMENTAL RESULTS

The above theory was tested in an apparatus described in ref. (3) on the system oxygen-magnesium oxide. The sum  $(2R'' + R')$  is immediately available from the slope of  $\log(w - w_\infty)/(w_0 - w_\infty)$  vs.  $t$  plot (Fig. 1) and amounts to  $2.02 \times 10^{18}$  molecules/min. At the same time, the linear relationship in these coordinates justifies the assumptions of the theory, namely it excludes heterogeneity and slow transport phenomena. The best fit of Eq. (13) to the experimental points is obtained for MgO when  $R''$  is put equal to  $5.05 \times 10^{17}$  molecules/min,  $R'$  to  $1.10 \times 10^{18}$  molecules/min, and  $R \approx 0$

(curve 3, Fig. 2). This fitted curve falls between the two limiting cases, (1)  $R'' = 0$ ,  $R' \neq 0$ ,  $R \neq 0$  (curve 1, Fig. 2), and (2)  $R'' \neq 0$ ,  $R' = R = 0$  (curve 2, Fig. 2). The value of  $2R'' + R' = 2.02 \times 10^{18}$  molecules/min is respected in all these considerations.

In the coordinates  $y^2/xz$  vs.  $t$  the two limiting cases are represented by curves 1 and 2 in Fig. 3. Theoretical curve 3 for  $R'' = 5.05 \times 10^{17}$  molecules/min,  $R' = 1.01 \times 10^{18}$  molecules/min and  $R \approx 0$  again agrees very well with experiment. Evidently, the change of  $y^2/xz$  with time, showing the minimum in Fig. 3, is a property of the exchange of one

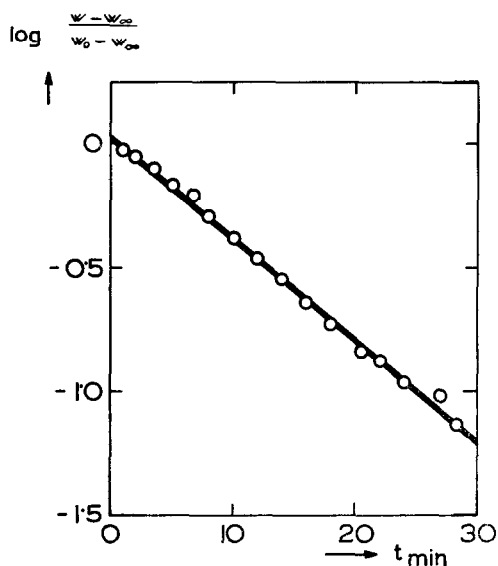


FIG. 1. Exchange of  $O^{18}$  between  $O_{2(g)}$  and  $MgO$ . Temperature,  $470^{\circ}C$ ; pressure of oxygen, 17 mm Hg;  $a = 2.67 \times 10^{19}$  molecules,  $m = 2.26 \times 10^{20}$  atoms,  $c = 1.006 \times 10^{19}$  atoms,  $w_0 = 9.61 \times 10^{18}$  atoms,  $y_0^2/x_0z_0 = 4$ ;  $(2R'' + R') = 2.02 \times 10^{18}$  molecules/min.

oxygen molecule with two oxygen atoms in the solid (rate  $R'' \neq 0$ ). It is interesting to

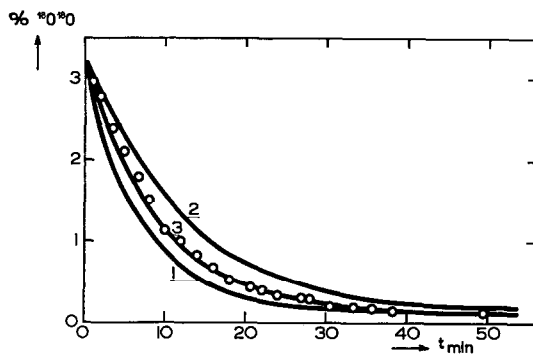


FIG. 2. Theory: curves 1, 2, and 3 as described in text;  $\circ$ , experimental points.

notice that in this case the equilibrium in the gas phase is first abolished and then in the last stages of exchange re-established.

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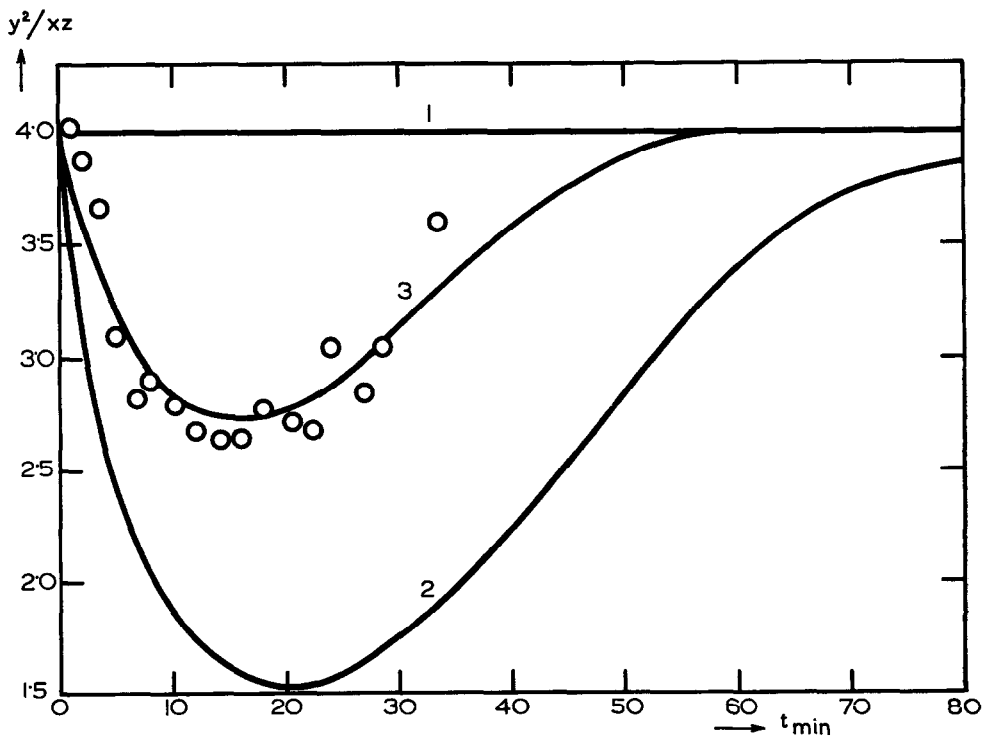


FIG. 3.  $y^2/xz$  vs. time. Theory: curves 1, 2, and 3 as described in text;  $\circ$ , experimental points.