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Interpretation of Isotope Exchange Data "without Time": Nonisothermal Exchange of Dioxygen with Oxides[1]

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Abstract—As a result of transformation of isotope-exchange rate equations (isotope-kinetic equations), a relationship was derived that does not contain time and universally relates the variables of isotope composition (an isotope-mechanistic equation). With the use of this relationship, mechanistic parameters that characterize atomic rearrangements can be determined from experimental data even in cases when the rate of exchange varied in the course of a process, for example, under nonisothermal conditions. The use of the proposed approach for the treatment of the results of dynamic thermal isotope exchange in the O_2–$YBa_2Cu_3O_y$ and O_2–Pt/CeZrO systems demonstrated that the experimental data were excellently described by the theoretical equation derived in this work

INTRODUCTION

Let us consider the following situation: A laboratory experiment on the isotope exchange of a diatomic (or polyatomic) gas was performed with sampling into ampules at regular intervals. On the way to a mass spectrometer, the ampule numbers were confused so that the time of sampling became unknown (the "loss of time" may also occur for other reasons). Is it possible in this case to obtain useful information on the exchange processes from the analysis of the isotope composition of gas samples? If possible, what information can be obtained and how? This work was devoted to answering these questions.

First, we cannot skip the reasonable question; what is lost together with time? The answer is obvious: the rate of process is lost in this case. Fortunately, this is the only loss (which is sometimes not the most serious loss, because the rate itself gives no information on the process mechanism). The rigorous theory of isotope kinetics [1–5] reveals crucial characteristics of an atomic and molecular process mechanism, which are inaccessible to other methods; they are often more important than the rate. A case in point is the rearrangements of atoms and atomic groups; these rearrangements can be characterized quantitatively [1, 5], and they are the essence of a chemical process. Thus, isotope kinetics methods make it possible not only to determine the intensity of a process but also to characterize its internal structure. Thus, by analogy, the velocity of a train can be judged by observing it from the outside or by looking into the window of the wagon. Of course, time is a necessary criterion in this case. However, all "the inte-

rior life" of passengers, in particular, their migrations (singly or in groups) among cars or compartments, is independent of the velocity of the train (except, of course, for accidents).

The interpretation of isotope data for situations in which no defined values of the rate of a process are available and the time dependence of the isotope composition cannot be described by analytic functions (rate equations) is considered below. The proposed approach was tested using the nonisothermal isotope exchange of dioxygen with some oxides as an example.

TYPES OF EXCHANGE MECHANISMS: VARIANTS OF MOLECULAR FRAGMENTATION AND ISOTOPE-KINETIC EQUATIONS

With the infinite manifold of conceivable reaction mechanisms in a particular chemical system, there is a limited and strictly determined set of atomic rearrangements (types of mechanisms) generated by a finite set of possible variants of molecular fragmentation [1, 5]. With any mechanism, the occurrence of a forward reaction resulted in the cleavage of the molecules of a component into fragments, which became the constituents of the resulting species, whereas the molecules of the initial component were formed from the same fragments in reverse reactions. In this case, the fragments can be constituents of both another component and intermediate species, the amount of which is immeasurably small compared with the amount of components.

The number of fragmentation variants depends on the atomicity of molecules and on the number of components. For a two-component system consisting of diatomic molecules A_2 in contact with another compo-

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[1] Dedicated to the memory of G.K. Boreskov.

Types of exchange mechanisms and variants of the fragmentation of diatomic molecules in the A_2–(A) system

j	Variant of fragmentation	Isotope exchange reaction	Mechanistic parameters	
			$a_1(j)$	$a_2(j)$
1	$A_2 + 2Z \rightleftharpoons 2ZA$	$X_2 + Y_2 \rightleftharpoons 2XY$	0	0
2	$A_2 + Z + (\ ) \rightleftharpoons ZA + (A)$	$X_2 + (Y) \rightleftharpoons XY + (X)$	0.5	0
3	$A_2 + 2(\ ) \rightleftharpoons 2(A)$	$X_2 + 2(Y) \rightleftharpoons Y_2 + 2(X)$	1	1

nent (partner) containing the same atoms (A), three (and only three) variants of fragmentation are possible, which are responsible for three possible types of process mechanisms depending on the entry of atoms into the composition of the partner (A) or intermediate species ZA (table) [6–8]. Here, the symbols (A) and ZA denote a generalized partner (the macroscopic amount of atoms A in the partner is commensurable or greater than that in the diatomic gas) and a generalized intermediate compound (the macroscopic amount of atoms A in which is immeasurably small as compared with the diatomic gas).

Note that the variants of fragmentation are represented in the table as conditional "reactions," which cannot be assigned a mechanistic meaning. That is, (A) and ZA are not necessarily monatomic species with respect to A (or structural elements of components); they may also contain other atoms (not only A). Correspondingly, ( ) and Z symbolize the above formations without an A atom (i.e., the acceptors of these atoms; in particular, these can be vacant sites).

If A atoms are represented by two isotopes (X and Y, for example, ^{18}O and ^{16}O), three variants of fragmentation of A_2 molecules result in three independent isotope exchange reactions (third column in the table) in the X_2–(Y) two-component system with reversible processes [6–9].

The distribution of the isotope molecules X_iY_{2-i} ($i = 0, 1, 2$), which is characterized by the mole fractions x_i, is determined by two independent variables of the composition (isotope variables) because $x_0 + x_1 + x_2 = 1$. It is most convenient to use the quantities α and z as the isotope variables [6–9], which are determined from the mole fractions of isotope molecules by the relations

$\alpha = 0.5x_1 + x_2$ (the fraction of isotope X in A_2) and

$z = x_2 - \alpha^2$ (the deviation from a binomial distribution).

The redistribution of isotopes in this system is described by the strict isotope-kinetic equations [6–9]

$$(N/R)(d\alpha/dt) = -a_1\alpha \qquad (1)$$

and

$$(N/R)(dz/dt) = -z + a_2\alpha^2, \qquad (2)$$

where

$$a_1 = 0.5\kappa_2 + \kappa_3 \qquad (3a)$$

and

$$a_2 = \kappa_3. \qquad (3b)$$

Here, N is the number of A_2 molecules; t is time; R is the overall rate of exchange (molecules per unit time); a_1 and a_2 are mechanistic parameters; and $\kappa_j = R_j/R$ is the contribution of exchange of the jth type; in this case, $R = \Sigma R$ and $\Sigma\kappa_j = 1$ ($j = 1, 2, 3$).

For simplicity, we have restricted ourselves here to the case when the amount of A atoms in the diatomic gas A_2 is much lower than that of exchangeable atoms in the partner (A), and the partner does not contain isotope X. This restriction can be easily removed (the general form of isotope-kinetic equations was given elsewhere [6–9]).

Note that isotope-kinetic equations in the form presented (in terms of R, a_1 and a_2) are given for the first time (usually, the rates of various types of exchange R_1, R_2, and R_3 were used as constants [6–9]). This form of the equations is most convenient for the subsequent analysis.

The principal feature of isotope-kinetic equations is that the mechanistic parameters (a_1 and a_2) are among the kinetic constants (along with the rate of exchange R). These mechanistic parameters take strictly defined numerical values for each type of mechanism (table); in the general case, they are linear combinations of these values with coefficients equal to the contributions of exchange types (κ_i). Equations (3a) and (3b) are nothing other than the scalar products of the vectors of mechanistic parameters of "pure" types (last two columns in the table) by the vector of type contributions (κ_1, κ_2, and κ_3):

$$a_{1(2)} = \Sigma\kappa_j a_{1(2)}(j). \qquad (3c)$$

Equations (1) and (2) are widely used (since they were first derived in [9]) in the isotope studies of atomic and molecular activation mechanisms of diatomic (with respect to the exchanged element) molecules: O_2, H_2, N_2, CO_2, etc. Evidently, the condition for the applicability of these equations is the acquisition of data on the time dependence of the isotope variables α and z at constant values of w and N. This condition is fulfilled when isothermal experiments are performed in a closed chemically equilibrium (or steady-state) system.
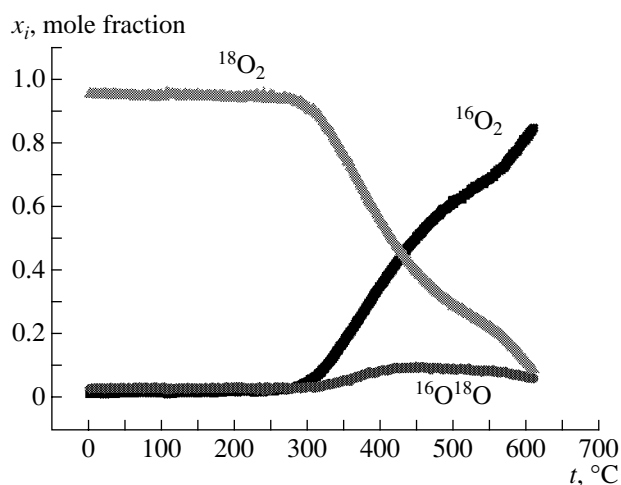
x_i, mole fraction

Fig. 1. Changes in the mole fractions (x_i) of isotope dioxygen molecules (52 Pa) in the O_2–$YBa_2Cu_3O_y$ system as the temperature is increased (10 K/min).

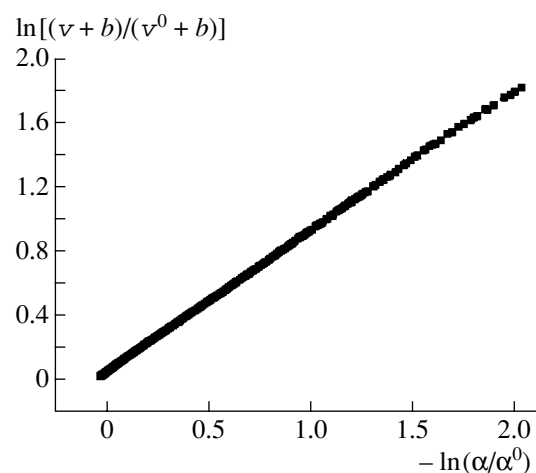$\ln[(v + b)/(v^0 + b)]$

Fig. 2. The experimental dependence of the isotope variables on the coordinates of isotope-mechanistic Eq. (4).

ISOTOPE-MECHANISTIC EQUATION AND ITS TESTING IN THE DYNAMIC THERMAL EXCHANGE OF DIOXYGEN WITH OXIDES

The condition for the applicability of isotope-kinetic equations cannot always be fulfilled; it is often specially violated by the design of experiments. In particular, this is true of commonly used temperature-programming techniques in kinetic studies (for example, see [10]). In these cases, there is no specific rate of exchange value, and the assignment of isotope variables to certain points in time cannot be used for the processing of experimental data.

However, the "loss" of time and rate does not exclude the possibility of determining the type of exchange. If the type of exchange remains unchanged in the course of a process, the mechanistic parameters a_1 and a_2 remain constant. The division of the latter equation by the former and the subsequent integration resulted in the following relationship between the isotope variables of the composition, which does not contain time and the quantities R and N:

$$\ln[(v + b)/(v^0 + b)] = -a\ln(\alpha/\alpha^0), \qquad (4)$$

where

$$a = (2a_1 - 1)/a_1 \qquad (5a)$$

and

$$b = a_2/(2a_1 - 1). \qquad (5b)$$

Here, the new isotope variable $v = z/\alpha^2$ (α^0 and v^0 are the initial values of the variables) is introduced for convenience.

It is reasonable to call this relationship an *isotope-mechanistic equation*.

A special version of this equation was derived and used previously [8].

If the type of the mechanism remains unchanged, Eq. (4) provides an opportunity to determine the mechanistic parameters and to calculate the contributions of exchange types from the experimental dependence of one isotope variable on another.

If experimental data cannot be described by Eq. (4), it can be convincingly concluded that the type of the mechanism is changed in the course of the process.

The proposed technique was applied to the interpretation of experimental data in the studies of isotope exchange of dioxygen with $YBa_2Cu_3O_y$ and Pt/Ce–Zr–O oxides by the dynamic thermal method (the experimental setup and procedure were described elsewhere [10]).
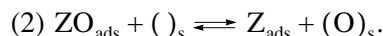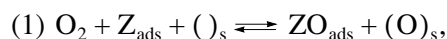
Figure 1 demonstrates the results of one of the experiments: changes in the isotopic composition of dioxygen (pressure of 52 Pa) in the O_2–$YBa_2Cu_3O_y$ system as the temperature is increased (10 K/min). As can be seen in Fig. 2, these data are excellently described by isotope-mechanistic Eq. (4). Analogous results were also obtained in other experiments.

The results obtained suggest that the type of the exchange mechanism in the test system remained unchanged as the temperature was changed.

For the experiment illustrated in Figs. 1 and 2, we determined the contributions of exchange types $\kappa_1 = 0$, $\kappa_2 = 0.2$, and $\kappa_3 = 0.8$ from the found values of parameters a and b with the use of Eqs. (3) and (5).

The relation between exchange types and possible process mechanisms (the nature of steps and the ratio between their rates) was considered in detail elsewhere [6–8].

The results obtained are consistent with the most widespread two-step mechanism of dioxygen exchange with oxides [6, 7]:

(1) $O_2 + Z_{ads} + ()_s \rightleftharpoons ZO_{ads} + (O)_s$,

(2) $ZO_{ads} + ()_s \rightleftharpoons Z_{ads} + (O)_s$.

The weakly bound adsorbed oxygen species ZO_{ads} and the strongly bound oxygen $(O)_s$ of the surface oxide layer participate in this mechanism.

If this mechanism takes place, the exchange of the first type is absent, whereas the contributions of the second and third types of exchange depend on the ratio between the rates of steps:

$$\kappa_2 = \rho_1/(\rho_1 + \rho_2) \quad \text{and} \quad \kappa_3 = \rho_2/(\rho_1 + \rho_2).$$

Here, ρ_i ($i = 1, 2$) is the single-direction rate of the ith step at equilibrium (i.e., the rate of the forward or reverse reaction under conditions when they are equal to each other).

Thus, in the experiment analyzed, $\rho_2/\rho_1 = \kappa_3/\kappa_2 = 4$.

In conclusion, note that nonisothermal and isothermal experiments should be combined to make better judgments about the mechanism of exchange. The proposed approach has still not been applied to the latter. However, there is no question that it will also be very helpful in that case, particularly, when the exchangeable oxygen atoms of an oxide are nonequivalent (as a consequence of surface heterogeneity or self-diffusion to the bulk).

ACKNOWLEDGMENTS

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