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Reaction Kinetics of Oxygen Heteromolecular Exchange with a Biographically Heterogeneous Surface

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Equations have been derived for describing the reaction rate of oxygen heteromolecular exchange with oxide catalysts within the framework of Temkin's model for a biographically heterogeneous surface. Data on the kinetics of exchange with V_2O_5 are used to illustrate application of these equations. A simplified model has been developed which relates the heteromolecular exchange rates to the observed activation energies and oxygen reaction orders for oxide systems.

INTRODUCTION

The kinetics of heteromolecular exchange reactions in gaseous oxygen–solid oxide systems are often studied to evaluate the strength of the surface oxygen bonding (*1*, *2*). A number of relationships have been found that relate the observed activation energies of the heteromolecular exchange (E_{O_2}) on the one hand, and properties of the catalysts such as the rates (*1*, *3*), rate constants (*1*, *3*), and their temperature dependences (*1*, *4*) for certain oxidation reactions, on the other hand. These relationships, however, are qualitative rather than quantitative since they are derived from the experimental data assuming that the oxide catalyst has a homogeneous surface. But the results of direct studies on catalysts often indicate that the reactivity and the strength of oxygen bonding depend to a noticeable extent on the oxygen coverage of the oxide surface. This is illustrated by calorimetric (*5*), thermodesorption (*6*), and pulsed kinetic results (*5*, *7*).

These data suggest that the surface oxygen of oxides is not homogeneous with respect to its reactivity or bond strength. Since heteromolecular exchange is accompanied by rupturing and formation of oxygen–catalyst bonds, the catalyst surface may exhibit heterogeneity in this reaction.

Muzykantov and Panov (*8*, *9*) have recently studied the reaction kinetics of heteromolecular exchange on oxide catalysts with discrete inhomogeneity; that is, with a surface which the authors regarded as a finite set of various active centers. According to Ref. (*9*), the observed exchange rate is the sum of the partial rates of exchange at the centers of each type, whereas the observed activation energy and the oxygen reaction order are the weighted means of partial activation energies and orders, respectively. Such an approach imposes a limit on the number of active center types. Apparently, this number should be small since only in this case is there a real possibility for analyzing the experimental data within the framework of the additivity model. Moreover, in this approximation, the observed kinetic parameters (the activa-

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tion energy and the reaction order for oxygen) should largely depend on the reaction conditions and the degree of exchange.

This study is an attempt to derive and analyze the parameters of the equations which describe the exchange rate in terms of Temkin's model for a biographically inhomogeneous surface (*10, 11*). Our kinetic equations are in good agreement with the experimental observations. We have made use of them to construct a simple model which relates the reaction rates to the activation energies and the oxygen reaction orders for heteromolecular exchange reactions with various oxides.

THEORETICAL

The kinetics of oxygen heteromolecular exchange reactions are usually studied in a steady state (equilibrium state) of the molecular oxygen–oxide system. We shall assume a steady state in which the rate of oxygen absorption by the oxide equals the rate of oxygen return to the gaseous phase. To reach this state the sample after an appropriate thermovacuum cleaning is exposed for a long time to oxygen at the partial pressure (P_{O_2}) and temperature T planned for measuring the heteromolecular exchange rate. The isotopic composition of oxygen is then instantaneously altered in the gaseous phase (a possible method for such alteration is described in the Experimental section of this paper). Oxygen atoms of a certain atomic weight (for instance, ^{18}O) will be referred to as labels. The label is transported between the phases owing to the differences in the isotope concentrations in the gaseous phase and on the oxide surface while the oxygen pressure in the system and the oxygen content in the surface layer remain constant. The label transport rate is, generally, an integral property of all the surface. If the surface is inhomogeneous and a continuous parameter h is used to describe the capacity of the surface centers for the heteromolecular exchange reactions, then the label transport rate ρ at any time instant is given by the following equation (*8*):

$$\rho = -\frac{N}{S}\frac{d\chi}{d\tau} = \frac{1}{L}\int_0^H r(h) \times[\chi - \chi_s(h)]\varphi(h)dh. \quad (1)$$

Here L is the total number of centers per unit surface area; $r(h)$ is the specific exchange rate for centers with the parameter h; χ and $\chi_s(h)$ are the current label fractions in the gaseous phase and in the exchange products at surface sites characterized by the parameter h; $\varphi(h)$ is the distribution function of centers over this parameter; H is the total variation range of h; N is the amount of oxygen in the gaseous phase; and S is the catalyst surface area.

When all exchangeable oxygen atoms of the oxide are equivalent (that is, χ_s is independent of h), the label transport rate is related to the total specific exchange rate R:

$$R = \frac{1}{L}\int_0^H r(h)\,\varphi(h)dh \quad (2)$$

by the following equation:

$$\rho = R(\chi - \chi_s). \quad (3)$$

Using Eq. (3) we can calculate R at any instant of time from the experimental values of ρ and χ and the value of χ_s found from the material balance equation. We shall not discuss here the experimental evaluation of χ_s or the merits and demerits of Eq. (3) over its integral time form as these problems are not essential for our study.

The fact that R is constant with time for given P_{O_2} and T is assumed to testify to the equivalence of exchangeable oxygen of oxide and vice versa. It should be stressed, however, that the concept of oxygen equivalence is not equivalent to the concept of surface homogeneity. Exchangeable oxygen is equivalent also on an inhomogeneous surface if fast processes (for instance, surface diffusion) level out the label concentration at each instant of time at all types of sites (*8*). When such equalization does not occur it is difficult to determine R from the experimental relationship between χ and τ. [Muzykantov and Panov (*8*) give the general form of the respective integro-differential equations and analyze their possible numerical solutions.] A possible qualitative approach to this problem is discussed in part II of this section. The remaining equations in this paper have been derived assuming the equivalence of exchangeable oxygen. The surface heterogeneity should then be expressed only by the analytic form of integral (2), that is, as a dependence of R on P_{O_2}, T, and the rate constants of elementary stages.

I. Exchangeable Oxygen is Equivalent

A. Oxygen adsorption without dissociation. Consider the simplest exchange mechanism. An oxygen molecule coming from the gaseous phase is adsorbed at a vacant surface site and one of the adsorbed molecules is desorbed into the gaseous phase (adsorption–desorption mechanism). We shall attach a meaning to the terms "adsorption" and "desorption" wider than it is customary in chemical kinetics. Any particle on a catalyst surface will be called adsorbed, even if it is indistinguishable from the regular oxygen ions in the oxide lattice. In the steady state defined above the mechanism

$$\begin{aligned} &\text{(i)} \quad Z + O^*_2 \xrightarrow{k_a} ZO^*_2 \\ &\text{(ii)} \quad ZO_2 \xrightarrow{k_d} Z + O_2 \end{aligned} \tag{4}$$

corresponds on the homogeneous surface to the exchange rate (the rate of adsorption or desorption at equilibrium)

$$R = k_a P_{O_2}(1 - \theta_{O_2}) = \frac{k_a k_d P_{O_2}}{k_d + k_a P_{O_2}}. \tag{5}$$

Here Z is a free center on the surface, O^*_2 is an oxygen molecule containing a labeled atom, k_a and k_d are the rate constants of adsorption and desorption, respectively, and θ_{O_2} is the surface area fraction occupied by oxygen.

The kinetic Eq. (5) yields the following expressions for E_{O_2} (observed exchange activation energies) and the reaction order n for oxygen:

$$E_{O_2} = \frac{1}{\tilde{R}} \cdot \frac{\partial \ln R}{\partial\left(-\dfrac{1}{T}\right)} = (1 - \theta_{O_2})E_a + \theta_{O_2}E_d, \tag{6}$$

$$n = \frac{\partial \ln R}{\partial \ln P_{O_2}} = 1 - \theta_{O_2} = \frac{k_d}{k_d + k_a P_{O_2}}, \tag{7}$$

where $\tilde{R}$ is the gas constant. Equations (6) and (7) show that E_{O_2} and n are functions of P_{O_2} and T.

Now consider the function R (P_{O_2}, T) in terms of Temkin's model (*10*) for a biographically heterogeneous surface. The surface center will be characterized by the oxygen adsorption heat. We shall assume, as required in the model, that the rate constants of adsorption k_{ai} and desorption k_{di} at the center i are expressed by

$$k_{ai} = \kappa_a \exp(-\alpha\lambda_i), \tag{8}$$

$$k_{di} = \kappa_d \exp(\beta\lambda_i). \tag{9}$$

Here and onward λ_i stands for the reduced desorbability factor which is equal to the difference between the maximum $\bar{Q}_a$ and the adsorption heats Q_{ai} of the oxygen molecule divided by $\tilde{R}T$ characteristic for a given center; κ_a and κ_d are the rate constants of adsorption and desorption at the sites with maximum adsorption heat, that is, at $\lambda = 0$; α and β are the transport coefficients, which are common fractions the sum of which is unity. As a rule, it is assumed that $\alpha = \beta = 0.5$ (*11*).

Thus, the exchange rate for the center i is a function of λ and is described by the following equation:

$$r(\lambda) = \frac{\kappa_a \kappa_d e^{(\beta-\alpha)\lambda} P_{O_2}}{\kappa_d e^{\beta\lambda} + \kappa_d e^{-\alpha\lambda} P_{O_2}}. \tag{10}$$

The constants κ_a and κ_d in (8) and (9) obey the Arrhenius law:

$$\kappa_a = \kappa_a{}^0 \exp(-\bar{E}_a/\tilde{R}T), \tag{11}$$

$$\kappa_d = \kappa_d{}^0 \exp(-\bar{E}_d/\tilde{R}T). \tag{12}$$

(The dash over the symbol indicates that the parameter relates to sites with maximum adsorption heat $\bar{Q}_a$.) It is assumed that $\kappa_a{}^0$ and $\kappa_d{}^0$ are identical over the whole surface.

Let us assume also that the distribution function of centers over λ may be approximated by the following equation (*10, 11*):

$$\varphi(\lambda) = A \exp(\gamma\lambda), \tag{13}$$

where A is a constant determined from normalization condition

$$\int_0^f \varphi(\lambda) d\lambda = L, \tag{14}$$

and γ is an index which varies from -1 to $+1$ and is proportional to T (*11*) so that its product with f does not depend on temperature, and f is the maximum value of λ.

To derive an equation for the exchange rate on the whole surface, the product of (10) and (13) should be integrated over λ:

$$R = \frac{1}{L} \int_0^f \frac{\kappa_a \kappa_d P_{O_2} e^{(\beta-\alpha)\lambda} A e^{\gamma\lambda} d\lambda}{\kappa_d e^{\beta\lambda} + \kappa_a P_{O_2} e^{-\alpha\lambda}}. \tag{15}$$

Using the mean coverage approximation (*10*), that is,

$$\begin{aligned} \theta_{O_2}|_{\lambda=0} &= \frac{\kappa_a P_{O_2}}{\kappa_d + \kappa_a P_{O_2}} \approx 1, \\ \theta_{O_2}|_{\lambda=f} &= \frac{\kappa_a P_{O_2} e^{-\alpha f}}{\kappa_d e^{\beta f} + \kappa_a P_{O_2} e^{-\alpha f}} \approx 0, \end{aligned} \tag{16}$$

we find that integral (15) yields the following equation (*10–12*):

$$R = \frac{\pi\gamma}{(e^{\gamma f} - 1) \sin(n\pi)} (\kappa_a P_{O_2})^n (\kappa_d)^m, \tag{17}$$

where n and m are common fractions: $m = \alpha - \gamma$ and $n = \beta + \gamma$. Equation (17) readily yields

$$E_{O_2} = n\bar{E}_a + m\bar{E}_d = \bar{E}_a + (1 - n)\bar{Q}_a. \tag{18}$$

Since n (17) does not depend on P_{O_2} and is weakly dependent on T, E_{O_2} is therefore almost independent of these parameters.

Let us also write the observed preexponential factor

$$k_{obs}{}^0 = \frac{\pi\gamma}{(e^{\gamma f} - 1) \sin(n\pi)} (\kappa_a{}^0)^n (\kappa_d{}^0)^m. \tag{19}$$

A particular case is a surface for which $\gamma = 0$ [it corresponds to Temkin's isotherm (*13*)]. When $\gamma \rightarrow 0$,

$$R = \frac{1}{f} (\kappa_a P_{O_2})^\beta (\kappa_d)^\alpha, \tag{20}$$

$$E_{O_2} = \bar{E}_{O_2} + \alpha\bar{Q}_a, \tag{21}$$

$$k_{obs}{}^0 = \frac{1}{f} (\kappa_a{}^0)^\beta (\kappa_d{}^0)^\alpha. \tag{22}$$

B. Adsorption of oxygen with dissociation. A mechanism is possible for exchange in which the oxygen molecule dissociates on adsorption and occupies two sites on the surface while desorption occurs via recombination of two atoms:

$$\begin{aligned} &\text{(i)} \quad 2Z + O^*_2 \xrightarrow{\kappa_a} 2ZO^*, \\ &\text{(ii)} \quad 2ZO \xrightarrow{\kappa_d} 2Z + O_2. \end{aligned} \tag{23}$$

For dissociative gas adsorption two approximations are used in Temkin's model: "spot" heterogeneity (*14*) and "random" heterogeneity (*15*). The former approximation assumes that the centers with identical adsorption heats form large clusters (effect of impurities) and two neighboring centers of dissociative adsorption have a high probability of being characterized by the same λ. In the latter approximation each of two centers is characterized by its own, generally random, λ. Kinetic equations for both approximations have been derived in the Appendix.

The resulting equations show that there is no significant kinetic difference between heteromolecular exchanges with a heterogeneous surface via dissociative adsorption [see Eq. (A6) and (A10) in the Appendix] and nondissociative adsorption [see Eq. (17)]. For instance, the exchange rate has the same dependence on the partial oxygen pressure in all the three cases and it does not discriminate between the exchange mechanism. Equation (18) holds valid for all the three cases. Some differences exist in the preexponential factors, but since they do not exceed one order of magnitude, they can be neglected in the approximate analysis and a simpler Eq. (19) may be used for evaluations and comparison with the experimental data. The similarity of the kinetic equations discussed above suggests also that Eq. (3) is exactly satisfied for those cases when the exchange proceeds via more than one mechanism simultaneously. The only essential requirement is that each of these mechanisms be an adsorption–desorption one.

C. Other Mechanisms. The following process illustrates the kinetics of heteromolecular exchange when the mechanism involves other stages besides adsorption and desorption:

$$\begin{aligned} &\text{(i)} \quad ZO + O^*_2 \rightleftharpoons ZOO^*_2, \\ &\text{(ii)} \quad ZOO^*_2 \rightleftharpoons ZO^*O_2, \qquad (24) \\ &\text{(iii)} \quad ZO^*O_2 \rightleftharpoons ZO^* + O_2. \end{aligned}$$

Here ZO denotes a surface oxygen atom which has a special position in the three-atom complex ZOO_2. When exchange occurs via such a mechanism, the label at the surface is a part of three particles, ZO^*, ZO^*O_2, and ZOO^*_2. The material balance equation yields only the total number of labeled atoms which have left the gaseous phase but not the label concentrations in each of the particle forms. If we assume that the exchange mechanism consists in the label being transported from the molecule O^*_2 to the particle ZO and that the particles ZO^*O_2 and ZOO^*_2 are intermediates in this transport, then the mechanism (24) may be considered as a single-route one. The general approach developed by Temkin in Ref. (*16*) can be applied here. In particular, for this mechanism the label transport rate is expressed by

$$\rho = \frac{r_1 r_2 r_3 \chi - r_{-1} r_{-2} r_{-3} \chi'_s}{r_2 r_3 + r_{-1} r_3 + r_{-1} r_{-2}}, \qquad (25)$$

where r_i is the rate of the forward stage, r_{-i} is the rate of the reverse stage, and χ'_s is the label concentration in the particles ZO. Ignoring the kinetic isotope effect and taking into account the steady-state condition we find

$$r_1 = r_{-1} = r_3 = r_{-3}$$

and

$$r_2 = r_{-2} \qquad (26)$$

Then we obtain

$$\rho = \frac{r_1 r_2}{2r_2 + r_1} (\chi - \chi'_s). \qquad (27)$$

When $r_2 \gg r_1$ we obtain the adsorption–desorption mechanism. When $r_1 \gg r_2$ we find

$$\rho = r_2(\chi - \chi'_s) = R(\chi - \chi'_s), \quad (28)$$

where R is the rate of redistribution of oxygen atoms within the three-atom complex. It is

$$R = k_2 \theta, \qquad (29)$$

where k_2 is the rate constant of stage (ii) in any direction for the mechanism (24), and θ is the surface coverage of the three-atom complexes.

Assuming that k_2 is the same for all surface centers we can derive a simple equation for the rate of heteromolecular exchange at the heterogeneous surface for this mechanism. Then we can replace the equilibrium coverage of the surface by oxygen θ in (29) by an appropriate equation (for instance, by the Temkin or the Freundlich isotherm).

II. Exchangeable Oxygen is not Equivalent

Oxygen adsorption without dissociation. If the exchangeable oxygen of the oxide is not equivalent, an equation of type (1) should be integrated

$$\rho = \frac{1}{L}\int_0^f r(\lambda)[\chi - \chi_s(\lambda)]\varphi(\lambda)d\lambda. \quad (30)$$

This can be done, for instance, by assuming an appropriate analytic approximation for $\chi_s(\lambda)$. The result is, of course, only qualitative.

Let us assume that this approximation given at any instant of time by the following relation:

$$\chi_s(\lambda) = 2\frac{\lambda}{f}X_s, \quad (31)$$

where X_s is the fraction of label on the surface when the exchangeable oxygen is equivalent. Equation (31) assumes that the sites with maximum adsorption heat ($\lambda = 0$) practically do not desorb oxygen of the initial isotope composition and therefore the label concentration at them is close to zero. On the contrary, the sites with minimum adsorption heat ($\lambda = f$) readily exchange the initial oxygen and the label fraction at the adsorbed state here is maximum. Approximation (31) is applicable, obviously, if $\chi_s < \chi$ (or $X_s < \frac{1}{2}\chi$).

Let us derive an equation for the label transport rate in the case of nondissociative oxygen adsorption.

Substituting Eqs. (10), (31), and (13) into (30) we find, using the mean coverage approximation [condition (16)],

$$\rho = R\left[\chi - \frac{2}{f}\left(\ln\frac{\kappa_a P_{O_2}}{\kappa_d} - \pi \cot(n\pi)\right)X_s\right], \quad (32)$$

where R is given by Eq. (17).

Thus, with the above approximations the correction factor which takes into account nonequivalence of the exchangeable oxygen is a function of P_{O_2} and T, but its magnitude is close to unity (at least for those oxides for which $n \leqslant 0.25$). Note that the possible introduction of an appropriate correction factor to account for nonequivalence of the exchangeable oxygen was in fact discussed in (*9*). However, the authors of (*9*) did not evaluate the range of variation of this factor. It is important to stress that, since this correction is close to unity, equations of the type of (30) are hardly sensitive to equivalence or nonequivalence of exchangeable oxygen for small degree depths.

Equations of the type of (32) may be derived also for the case of adsorption with dissociation. However, the approximation suggested in (*17*), rather than (31), is more appropriate in this case.

EXPERIMENTAL

Isotope oxygen exchange with vanadium pentoxide was studied. At low pressures (up to 5 Torr) the exchange was carried out in a static system with natural circulation of gases. First we verified that mass transfer phenomena did not limit the exchange rate. At oxygen pressures exceeding 5 Torr, the exchange reactions were studied in a static circulation system (*18*). Circulation was effected by means of a glass electromagnetic piston pump (*19*).

The isotopic composition of the reaction mixture was repeatedly analyzed with an MI-1305 mass spectrometer. The accuracy of the mass spectrometer analysis is estimated to be ±1% of the value measured. The test gas was delivered to the mass spectrometer ion source through a capillary.

Oxygen of natural isotopic composition was obtained by thermal decomposition of $KMnO_4$ and labeled oxygen by electrolytic decomposition of water enriched in isotope ^{18}O up to 40–50 atom%. Oxygen was purified from hydrogen admixture on Pd/Al_2O_3 and dried by means of molecular sieves NaX and 4A and a Petryanov filter (*20*) at the temperature of liquid nitrogen. The initial gas was an equilibrium mixture of isotopic molecules of oxygen $^{16}O^{16}O$, $^{16}O^{18}O$, and $^{18}O^{18}O$. The gas pressure drop due to sampling was not more than 10–15% at the end of the experiments.

The catalyst, vanadium pentoxide, was prepared from an analytical grade commercial sample by roasting for 6 hr at 500°C in an oxygen flow. The V_2O_5 powder was tableted, and the tablets were crushed into granules. For granules of 0.5- to 1-mm size, the efficiency factor was almost equal to unity practically over the whole range of experimental conditions. The specific surface of the V_2O_5 samples was about 2 m^2/g.

The catalyst sample was loaded into the reactor and evacuated for 4 hr at 400°C down to a pressure below 10^{-4} Torr. Then the sample was heated at 500°C for 6 hr in oxygen of natural isotopic composition under a pressure planned for the experiment. Two hours before the experiment, the temperature of the sample was reduced to the temperature of exchange. The isotopic composition of oxygen over the catalyst was altered as follows: The small reaction vessel with the catalyst sample (about 30 ml) was isolated from the rest of the system (630 ml) which was evacuated and filled with ^{18}O-enriched oxygen, the initial mixture was analyzed, and then the reaction vessel was evacuated for 10–20 sec and connected to the rest of the system. The pressure in the reaction vessel was reduced on evacuation by more than one order thus allowing us not to consider the gas remaining in the reaction vessel in determination of χ_0. In preliminary experiments it was established that with V_2O_5 the evacuation does not alter the specific activity of the oxide with respect to exchange as compared to the experiments carried out without preliminary evacuation prior to connection of the reaction vessel filled with natural oxygen to the circulation loop. The absence of any effect of short evacuation of the oxide on its activity in the heteroexchange reaction is, in our opinion, related to the rapid reversible alteration of the V_2O_5 surface oxidation degree that was observed by us when changing oxygen pressure over the oxide in the interval of 10^{-3}–600 Torr [the V_2O_5 surface oxidation degree was monitored by measuring the electron work function by the vibrating condenser technique (*21*)].

Oxygen heteromolecular exchange was studied at 410–505°C in the interval 0.4–560 Torr of oxygen pressure. A chromel–copel thermocouple was used for temperature control in the catalyst layer. The accuracy of temperature maintenance was ±1°C.

The heteromolecular exchange rate on V_2O_5 was found to obey Eq. (3) up to almost total equilibration of the oxygen isotopic composition in the gaseous phase and the whole of the oxide (Fig. 1); i.e., in this case χ_s is the label fraction of ^{18}O in the whole oxide bulk. This is explained by the fact that all the oxygen of oxide is equivalent with respect to exchange owing to high rates of oxygen self-diffusion. In fact, according to the authors' evidence (*22*) and the known literature data (*23*, *24*), the values of oxygen diffusion rates in V_2O_5 in the temperature range studied must exceed substantially (up to two orders) the corresponding values of the rates of oxygen heteromolecular exchange. When the pressure was varied from 0.2 to 100 Torr the order of oxygen exchange rate remained constant, close to $\frac{1}{2}$ (Fig. 2). Under the same conditions the exchange activation energy was 44 kcal/mol (Fig. 3). For pressures exceeding 100 Torr, the reaction order for oxygen decreases, whereas the exchange

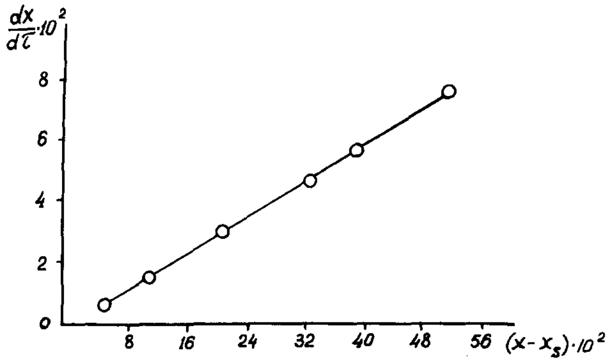

FIG. 1. Kinetics of heteromolecular oxygen exchange with vanadium pentoxide at 450°C.

activation energy increases (Table 1). Special experiments (450°C; $P_{O_2} = 6$ Torr) and calculations according to (*25, 26*) have shown that the heteromolecular exchange proceeds via the so-called III mechanism; that is, it involves two surface atoms.

The kinetic parameters found in this study and the suggested exchange mechanism are in good agreement with the results of authors (*27–31*).

DISCUSSION

There are two questions which we attempt to answer in this paper, namely:

1. Do our experimental results for vanadium pentoxide conform to our model of kinetics at a heterogeneous surface?
2. Can the model of heterogeneous surface be applied to other oxides?

Exchange involving two surface atoms is usually assumed to proceed via an adsorption–desorption mechanism involving molecular dissociation (*25*). The kinetic equation for this mechanism which describes the exchange rate at a homogeneous surface has the following form:

$$R = \frac{k_a k_d P_{O_2}}{([k_d]^{\frac{1}{2}} + [k_a P_{O_2}]^{\frac{1}{2}})^2}. \qquad (33)$$

The experimental data obtained at 490°C

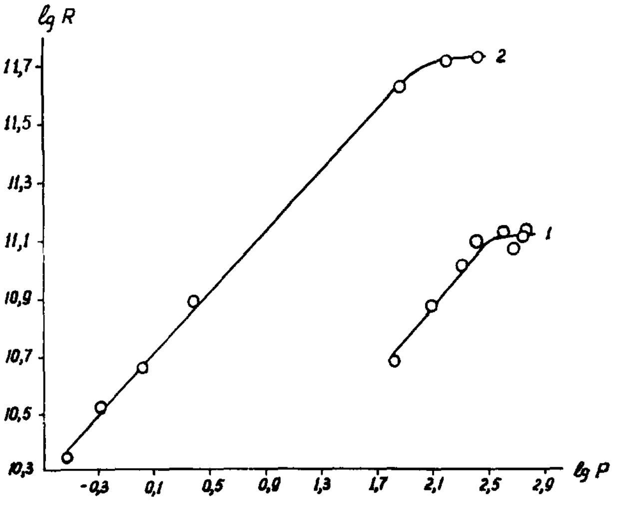

FIG. 2. Heteromolecular exchange rate of oxygen with vanadium pentoxide as a function of oxygen pressure: 1, 455°C; 2, 490°C.

TABLE 1

Kinetic Parameters of Heteromolecular Oxygen Exchange with Vanadium Pentoxide

P_{O_2} (Torr)	T (°C)	E_{obs} (kcal/mol)	R at 450°C (O$_2$ molec.)/(cm^2 s)	$k_{obs}{}^0$ (O$_2$ molec.)/(cm^2 s at.)	n at P_{O_2} (Torr) of 0.2–100	400–560
0.4	410–490	44	$5\cdot10^{9}$	$5\cdot10^{24}$	0.5	—
260	440–500	51	$6\cdot10^{10}$	$5\cdot10^{26}$	—	—
560	455–505	60	$1.3\cdot10^{11}$	10^{29}	—	0

are given in Fig. 4 in coordinates which correspond to a linearized form of Eq. (33). The deviations from the linear relationship are regular and exceed the possible experimental errors. On the contrary, Fig. 2 shows that these experimental data conform to an equation of the type of (A6) or (A10). Hence, the heterogeneous surface model provides a better description of the heteromolecular exchange rate as a function of the oxygen pressure than the homogeneous surface model.

Moreover, the homogeneous surface model [Eq. (33)] does not agree with the fact observed by us and other authors that the observed exchange activation energy is constant when the oxygen pressure is varied over a fairly wide range. For instance, when $P_{O_2} = 0.4$ Torr, $E_{obs} = 44$ kcal/mol (*32*); when $P_{O_2} = 11$ Torr, $E_{obs} = 47$ kcal/mol (*33*); when $P_{O_2} = 40$ Torr, $E_{obs} = 44$ kcal/mol (*28*); and when $P_{O_2} = 95.6$–101 Torr, $E_{obs} = 45$ kcal/mol (*27*).

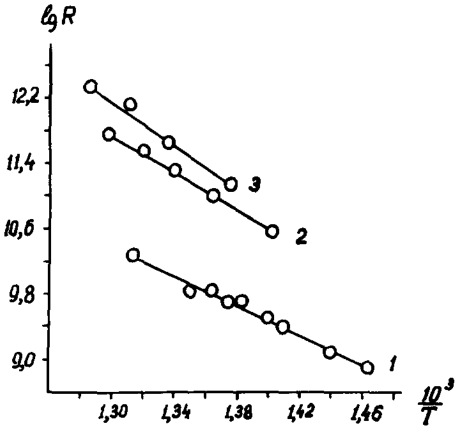

FIG. 3. Temperature dependence of the heteromolecular exchange rate of oxygen with vanadium pentoxide: 1, 0.4 Torr; 2, 260 Torr; 3, 560 Torr.

The kinetic Eq. (33) yields the following expression for E_{O_2}:

$$E_{O_2} = \frac{(k_d)^{\frac{1}{2}}E_d + (k_aP_{O_2})^{\frac{1}{2}}E_a}{(k_d)^{\frac{1}{2}} + (k_aP_{O_2})^{\frac{1}{2}}}. \qquad (34)$$

It can readily be shown that E_{O_2} under two different pressures can be the same

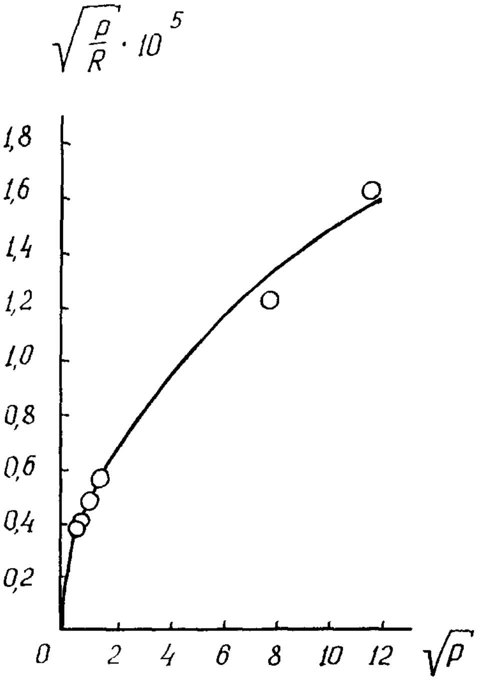

FIG. 4. A study of the validity of Eq. (33) (T = 490°C).

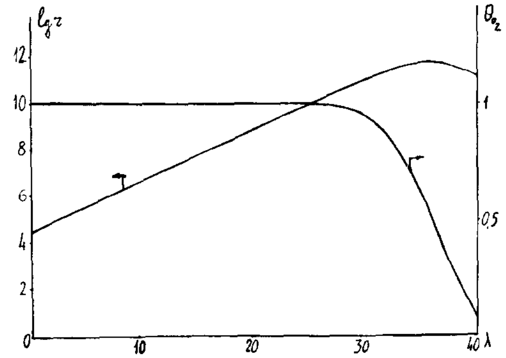

FIG. 5. Calculated curves for specific heteromolecular exchange at $P_{O_2} = 10^{-3}$ at and $T = 450°C$ as a function of desorbability λ.

only if the unlikely condition $E_a = E_d$ is satisfied (since this means that the adsorption heat is zero) or in the limiting cases when $k_d \gg k_a P_{O_2}$ or $k_a P_{O_2} \gg k_d$. But the experimental results on variation of oxygen pressure show that the ratio of these constants is close to unity. In other words, $(k_d)^{\frac{1}{2}}$ and $(k_a P_{O_2})^{\frac{1}{2}}$ are comparable under some partial pressures within the range studied by the above authors.

However, Eqs. (17), (A6), and (A11) show that E_{O_2} is independent of P_{O_2} when conditions (16) are satisfied. Thus, the temperature dependence of the heteromolecular oxygen–V_2O_5 exchange rate is also in a better agreement with the assumption about heterogeneity of the oxide surface.

Moreover, there are some direct data that show the heterogeneity of vanadium pentoxide.

Measurements of the temperature dependence of the equilibrium oxygen pressure over the oxide have shown that the bonding energy of surface oxygen increases from 20 to 70 kcal/mol (*34*) with an increasing degree of reduction of V_2O_5. The authors of (*35*) have also found the dependence of the bonding energy on the degree of reduction of V_2O_5. Heterogeneity of vanadium pentoxide surface is suggested also by the adsorption kinetics which are characterized by equations corresponding to the logarithmic (*36*) or exponential (*37*) isotherms depending on the previous treatment of the sample.

Now let us analyze Eq. (18). Note that we can measure only the first two of the four parameters in this equation: n, E_{O_2}, $\bar{E}_a$, and $\bar{Q}_a$. It is hard to measure $\bar{E}_a$ and $\bar{Q}_a$ since it is impossible, owing to diffusion from the oxide bulk, to maintain zero surface coverage with oxygen and stoichiometric ratio in the whole of the oxide.

One can assume arbitrarily that both parameters can be calculated from the data given in Table 1. Indeed, knowledge of n and E_{O_2} is formally sufficient for evaluating the remaining two parameters. But it should be remembered that alteration of the reaction order, according to the heterogeneous surface model, disrupts the mean coverage approximation so that equations of the type of (17) and (18) become inaccurate.

Thus, to make use of Eq. (18) we should preset one of the nonmeasurable parameters or, at least, specify how to preset it. It is more convenient to specify $\bar{E}_a$. Physically, this parameter should be close to the activation energy of oxygen adsorption on the pure metal; in other words, it should be rather close to zero. If we assume for simplicity that $\bar{E}_a = 0$, Eq. (18) transforms into

$$E_{O_2} = (1 - n)\bar{Q}_a. \qquad (35)$$

This yields

$$\bar{Q}_a = \frac{E_{O_2}}{1 - n}. \qquad (36)$$

Hence we calculate that for vanadium pentoxide $\bar{Q}_a = 85$ kcal/mol. This value is close to the strength of the metal–oxygen bonding in oxides and thus seems to be reasonable.

As reported for various oxide catalysts, the minimum oxygen adsorption heat varies from 20 to 25 kcal/mol (*35*, *38*). Hence, the heterogeneity range f at the temperature of about 450°C is $(85\text{–}25)\ \tilde{R}T = 40$. This heterogeneity range at $\alpha = \beta = 0.5$ corresponds to the maximum differences between the activation energies for adsorption and desorption for the surface centers $\Delta E = (85\text{–}25)\cdot\alpha = 30$ kcal/mol.

Let us now analyze the preexponential factor. If we assume $\alpha = \beta = 0.5$, then $n = 0.5$ means that $\gamma = 0$. In this case we should make use of Eq. (A7). Let us substitute into (A7) the theoretical preexponential factors of adsorption and desorption. In the temperature range studied the number of molecules striking unit surface area per second is about 10^{23} molecules/cm^2 s at and, according to the absolute rate theory (*39*), $\kappa_d{}^0$ varies from 10^{28} to 10^{30} molecule/cm^2 s. Let us assume $\kappa_d{}^0 = 10^{29}$ molecules/cm^2 s according to the experimentally determined value for the complete surface coverage, that is, for $n = 0$. Then the theoretical value of the observed preexponential factor is given by

$$k^0 = 2/40(10^{23})^{0.5}(10^{29})^{0.5}$$
$$= 5\cdot 10^{24} \text{ molecules/cm}^2 \text{ s at}^{\frac{1}{2}}$$

This estimate is in very good agreement with the experimental value (see Table 1). This agreement also supports the heterogeneous surface model rather than the homogeneous surface model. Moreover, it suggests a very important conclusion, namely, that heteromolecular exchange involves practically the whole surface of vanadium pentoxide since the theoretical value of the observed preexponential factor made use of the values related to the whole surface (10^{15} centers/cm^2).

Some explanation is needed here. The accuracy of the experimental estimate of $k_{\text{obs}}{}^0$ and, hence, of our conclusion is, of course, within one order of magnitude. Our values of the number of sites on the unit surface area and $\kappa_a{}^0$ and $\kappa_d{}^0$ are somewhat arbitrary, too.

Another factor should also be taken into account. The rate at the most active surface centers differs from the rate at the least active centers by seven or eight orders of magnitude (Fig. 5). This leads us to question whether we can call such a center active if it participates in the direct exchange with the gaseous phase once every 10^{11} s on the average (that is, during a period which is approximately equal to the life span of our civilization) while the surface contains centers which exchange their oxygen in 10^3 s. If the answer is no then what should be the difference between the rates for a given center and the optimum one? Any quantitative evaluation here would be, essentially, a matter of viewpoint. But our assumption that the exchange involves all the centers of the surface has no such disadvantage.

This assumption makes it possible to calculate, for instance, the integral oxygen coverage of the surface $\tilde{\theta}$. Since the surface of V_2O_5 is uniformly heterogeneous we shall estimate $\tilde{\theta}$ using Temkin's isotherm equation (*13*). For instance, for $P_{O_2} = 10^{-3}$ at and $T = 430$°C we find

$$\tilde{\theta} = \frac{1}{f}\ln\frac{\kappa_a P_{O_2}}{\kappa_d}$$
$$= \frac{1}{f}\ln\frac{\kappa_a{}^0 \exp[-\bar{E}_a/\tilde{R}T]P_{O_2}}{\kappa_d{}^0 \exp[-\bar{E}_d/\tilde{R}T]}$$
$$= \frac{1}{40}\ln\frac{10^{23}\cdot 10^{-3}}{10^{29}\exp[-85{,}000/\tilde{R}T]}$$
$$\approx 0.9. \quad (37)$$

Thus, the surface is almost completely covered with adsorbed oxygen even under such low oxygen pressures. Remember that we define the adsorbed atom as any oxygen atom at the surface including those atoms that are indistinguishable from the ions in the lattice.

Using Eqs. (16) we can show the mean coverage approximation to be invalid for V_2O_5 at $P_{O_2} = 3\cdot 10^{-1}$ at. Under these conditions we have $\theta_{O_2}|_{\lambda=f} \neq 0$ and $\tilde{\theta} \approx 1$.

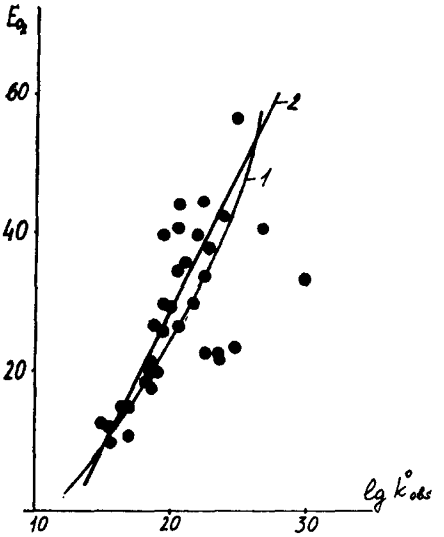

FIG. 6. Observed heteromolecular exchange activation energy E_{O_2} vs preexponential factor $k_{obs}{}^0$ (*2*): 1, calculations in terms of our model; 2, least-squares curve.

The data given in Table 1 agree with this prediction.

Now let us discuss if we can apply the heterogeneity model to describe the kinetics of the heteromolecular oxygen exchange with other oxides. We believe that the heterogeneity model may be applied to those many oxides for which the reaction order for oxygen remains constant when the oxygen pressure is varied by a few hundred percent. Moreover, let us assume that the minimum adsorption heats vary from 20 to 25 kcal/mol, that the maximum adsorption heats vary from 80 to 85 kcal/mol, that the adsorption activation energy at the sites with the maximum adsorption heat is zero, and that the whole of the surface is involved in the exchange; that is, $\kappa_a{}^0 = 10^{23}$ molecules/cm^2 s at. and $\kappa_d{}^0 = 10^{29}$ molecules/cm^2 s (their temperature dependence is not taken into consideration).

Let us analyze together Eqs. (36) and (19) in terms of this model. If we assume that $\alpha = \beta = 0.5$ we obtain

$$n = 0.5 + \gamma$$

and

$$m = 0.5 - \gamma, \tag{38}$$

and from (36) we find for the above parameter

$$\gamma = 0.5 - \frac{E_{O_2}}{80}. \tag{39}$$

Equation (39) does not conform to the linear relationship between γ and T postulated in the Temkin model (*11*). However, it is essential for the term $e^{\gamma t}$ to be independent of the temperature. By definition, f is inversely proportional to the temperature. Since we neglected the temperature dependence of γ we have to neglect the temperature dependence of f. Let us assume that f is 40 and remains constant. Then, according to Eqs. (19), (38), and (39) there should be a direct relationship between $k_{obs}{}^0$ and E_{O_2}. This relationship is plotted in Fig. 6. Also shown in this figure are the experimental data of Winter (*2*) and his straight line representing the least-square approximation. The theoretical curve is seen to agree with the experimental relationship between log $k_{obs}{}^0$ and E_{O_2}. It may be assumed that the differences in the values of n, E_{O_2}, and $k_{obs}{}^0$ (and, hence, R) between various oxides are probably due to the differences in the distributions of the centers over λ, that is, over oxygen adsorption heats [Eq. (13)].

Note that we have not attempted here to obtain the best approximation of the experimental results by a theoretical equation. The primary reason for this is that, in our opinion, Winter (*2*) made some methodological mistakes which could have influenced the results of the heteromolecular exchange rate measurements.

First, prior to filling the reaction vessel with the ^{18}O-enriched oxygen, Winter evacuated it for 3 min at the temperature of the experiment. According to our model, the activation energy of desorption at various surface centers ranges from 50 to 80 kcal/mol (since $\bar{Q}_a = 80$ kcal/mol, $\bar{E}_a = 0$, and $\Delta E = 30$ kcal/mol). The rate of desorption from the centers for which $E_d = 50$ kcal/

mol is given by

$$r_d = 10^{29} \exp[-50{,}000/\tilde{R}T]\theta_{O_2}.$$

Let us take $\theta_{O_2} = 10^{-1}$ (see Fig. 5) and $T = 450°C$. Then we find $r_d = 10^{13}$ molecules/cm^2 s; hence, all the centers with $E_d = 50$ kcal/mol desorb oxygen in about 2 min. A part of their oxygen is desorbed also by the centers with $E_d = 53$ kcal/mol which makes the primary contribution to the exchange rate for the oxides with $E_{O_2} > 40$ kcal/mol (Fig. 5). This loss of oxygen is compensated owing to the high rates of diffusion from the bulk of the oxide to its surface. On the contrary, evacuation of the sample for 3 min can introduce a serious error into the measured exchange rate for those oxides which have low oxygen diffusion rates and integral surface coverages close to unity.

The greatest error appears to be introduced by the preparation of the catalyst for determination of the reaction order for oxygen; the sample was kept at a given temperature and a pressure of 15 Torr for 18 hr and subsequently at least one measurement was made at 100 Torr (*2*). We have found earlier (*32*) that following prolonged heating at 10 Torr lower pressures (0.4 Torr) result in a noticeable desorption of oxygen from the surface to the gaseous phase. Hence, elevation of pressure should result in irreversible absorption of oxygen by the oxide. The error caused by this absorption is the greater the higher is the oxygen diffusion rate in the oxide and the lower the integral coverages at equilibrium.

Both mistakes in the procedure affect the estimates of the heteromolecular exchange rate owing to inaccurate determinations of χ_s [Eq. (3)] [or the amount of the exchangeable oxygen since Winter used the integral form of Eq. (3) when calculating R]. This is, probably, the reason why the values of n found in (*2*) do not agree with our predictions according to (38).

Another point has to be discussed, too. The heteromolecular exchange is usually studied under oxygen pressures varying from 10^{-3} to 1 at. This pressure difference has been shown above [Eq. (36)] to correspond to variation of the integral coverage from 0.9 to 1 on V_2O_5, that is, only by 0.1 of the monolayer. For other oxides the variation of the coverage may be different according to the value of γ, since the absolute values of θ strongly depend on this parameter. However, even in this case the primary contribution to the observed exchange rate is made by the centers with λ varying from 30 to 40, that is, within a limited variation range of the energy parameters. This is precisely what seems to allow the simple function (13) to make a good approximation of the real center distribution for the whole surface with regard to their activity in the heteromolecular exchange reaction.

APPENDIX

1. Let the surface be heterogeneous in "spots":

$$r(\lambda) = \frac{\kappa_a \kappa_d e^{(\beta-\alpha)\lambda} P_{O_2}}{([\kappa_d e^{\beta\lambda}]^{\frac{1}{2}} + [\kappa_a P_{O_2} e^{-\alpha\lambda}]^{\frac{1}{2}})^2}, \tag{A1}$$

$$R = \frac{1}{L}\int_0^f \frac{\kappa_a \kappa_d P_{O_2} e^{(\beta-\alpha)\lambda} A e^{\gamma\lambda} d\lambda}{([\kappa_d e^{\beta\lambda}]^{\frac{1}{2}} + [\kappa_a P_{O_2} e^{-\alpha\lambda}]^{\frac{1}{2}})^2}. \tag{A2}$$

Let us replace the variable:

$$\left(\frac{\kappa_a P_{O_2}}{\kappa_d} e^{-\lambda}\right)^{\frac{1}{2}} = u. \tag{A3}$$

Here we shall replace approximately the integration limits as it was done by Temkin in (*10*). When we have $\lambda = 0$ we find $u = (\kappa_a P_{O_2}/\kappa_d)^{\frac{1}{2}} \approx \infty$ (since for the sites with the adsorption heat $\bar{Q}_a$, κ_a is maximum and κ_d is minimum). When $\lambda = f$ we have $u = 0$. Both replacements correspond to the condition that the reaction be carried out in the range of mean coverages (*10*).

Then we obtain

$$R = \frac{2A}{L} \kappa_a P_{O_2} \left(\frac{\kappa_d}{\kappa_a P_{O_2}} \right)^{\alpha-\gamma} \times \int_0^\infty \frac{u^{2(\alpha-\gamma)-1} du}{(1+u)^2}. \quad \text{(A4)}$$

When

$$0 < m = \alpha - \gamma < 1,$$
$$0 < n = \beta + \gamma < 1, \quad \text{(A5)}$$

we have (*40*) the following expression for the integral (A4):

$$R = \frac{\gamma(1-2n)\pi}{(e^{\gamma f}-1)\sin(2n\pi)} (\kappa_a P_{O_2})^n (\kappa_d)^m. \quad \text{(A6)}$$

When $\gamma \rightarrow 0$ we find

$$R = \frac{2}{f} (\kappa_a P_{O_2})^\beta (\kappa_d)^\alpha. \quad \text{(A7)}$$

2. Let the surface be "randomly" heterogeneous (*15*):

$$\begin{aligned} &\text{(i)} \quad Z + Z_1 + O_2^* \xrightarrow{k_a} ZO^* + Z_1O \\ &\text{(ii)} \qquad ZO + Z_1O \xrightarrow{k_d} Z + Z_1 + O_2 \end{aligned} \quad \text{(A8)}$$

If the adsorption heats per one atom (that is, per a ZO bond) are q_a and q_{a_1} and their differences from the maximum value $\bar{q}_a$ are Δq_a and Δq_{a_1} the variations of the activation energies of the stages are given by the following relations:

$$\begin{aligned} \Delta E_a &= \alpha(\Delta q_a + \Delta q_{a_1}) = \alpha(\lambda' + \lambda'_1)\tilde{R}T \\ \Delta E_d &= -\beta(\Delta q_a + \Delta q_{a_1}) \\ &= -\beta(\lambda' + \lambda'_1)\tilde{R}T. \end{aligned} \quad \text{(A9)}$$

Since we have

$$r(\lambda) = \frac{\kappa_a \kappa_d P_{O_2} e^{(\beta-\alpha)\lambda'} e^{(\beta-\alpha)\lambda'_1}}{([\kappa_d]^{\frac{1}{2}} e^{\beta\lambda'} + [\kappa_a P_{O_2}]^{\frac{1}{2}} e^{-\alpha\lambda'})([\kappa_d]^{\frac{1}{2}} e^{\beta\lambda'_1} + [\kappa_a P_{O_2}]^{\frac{1}{2}} e^{-\alpha\lambda'_1})}, \quad \text{(A10)}$$

the exchange rate R is given by

$$\begin{aligned} R &= \frac{1}{L^2} \int_0^{f_a} \int_0^{f_a} \frac{\kappa_a \kappa_d P_{O_2} e^{(\beta-\alpha)\lambda'} e^{(\beta-\alpha)\lambda'_1} A^2 e^{\gamma\lambda'} e^{\gamma\lambda'_1} d\lambda' d\lambda'_1}{([\kappa_d]^{\frac{1}{2}} e^{\beta\lambda'} + [\kappa_a P_{O_2}]^{\frac{1}{2}} e^{-\alpha\lambda'})([\kappa_d]^{\frac{1}{2}} e^{\beta\lambda'_1} + [\kappa_a P_{O_2}]^{\frac{1}{2}} e^{-\alpha\lambda'_1})} \\ &= \frac{A^2}{L^2} \left(\int_0^{f_a} \frac{[\kappa_a \kappa_d P_{O_2}]^{\frac{1}{2}} e^{(\beta-\alpha)\lambda'} e^{\gamma\lambda'} d\lambda'}{[\kappa_d]^{\frac{1}{2}} e^{\beta\lambda'} + [\kappa_a P_{O_2}]^{\frac{1}{2}} e^{-\alpha\lambda'}} \right)^2 \quad \text{(A11)} \\ &\approx \left(\frac{\pi\gamma}{(e^{\gamma f_a}-1)\sin(n\pi)} \right)^2 (\kappa_a P_{O_2})^n (\kappa_d)^m. \end{aligned}$$

Here f_a is the heterogeneity interval per one atom. Physically, it may be expected that $f_a \approx \frac{1}{2} f$ though no obvious link exists between these parameters. Moreover, there is no obvious relationship between κ_a and κ_d in the case of dissociative and nondissociative adsorption. For the logarithmically homogeneous surface we have

$$R = \frac{1}{f_a^2} (\kappa_a P_{O_2})^\beta (\kappa_d)^\alpha. \quad \text{(A12)}$$

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