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Determination of the Rate Constants for the Reaction Fe + O_2 = FeO + O in the Forward and Reverse Directions

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Abstract—The results of our experimental studies and an analysis of the published data on the rate constant for the reaction Fe + O_2 = FeO + O in the forward (I) and reverse (–I) direction are reported. The data obtained in this work are described by the expressions $k_1 = 6.2 \times 10^{14}\exp(-11100\ \mathrm{K}/T)$ cm^3 mol^{-1} s^{-1} and $k_{-1} = 6.0 \times 10^{13}\exp(-588\ \mathrm{K}/T)$ cm^3 mol^{-1} s^{-1} (T = 1500–2500 K). The generalized expressions for the temperature dependences of these rate constants derived by combining our results with the literature data can be presented as $k_1 = 9.4 \times 10^{14}(T/1000)^{0.022}\exp(-11224\ \mathrm{K}/T)$ cm^3 mol^{-1} s^{-1} (T = 1500–2500 K) and $k_{-1} = 1.8 \times 10^{14}(1000/T)^{0.37}\exp(-367\ \mathrm{K}/T)$ cm^3 mol^{-1} s^{-1} (T = 200–2500 K).

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The interaction of iron atoms with molecular oxygen is of considerable interest both from the standpoint of fundamental studies of the reactivity of elements, and for a variety of applications [1–5]. In particular, a strong catalytic effect of small additives of iron pentacarbonyl on the oxidation of carbon monoxide by molecular oxygen was observed [1]. On the other hand, small additives of iron-containing compounds show a marked soot-suppressing effect [2] and a strong inhibitory influence on the combustion of hydrocarbon fuels [3, 4]. Iron and its oxides play an important role in atmospheric chemistry, especially, in connection with their impact on the ozone layer [6–9]. For this reason, information on the rate constants of the reactions occurring in the Fe–O_2 system, in particular for

$$\mathrm{Fe} + \mathrm{O_2} = \mathrm{FeO} + \mathrm{O} \qquad \text{(I)}$$

is of considerable interest.

A lower estimate of the rate constant of reaction (I) at 2400 K and a pressure of ~100 Torr was first obtained in [10]. Measurements at one temperature, 1600 K, and pressures of 15–60 Torr were carried out in [11]. A more detailed study of this reaction was conducted in [12, 13]. As shown in [12], iron atoms interact with molecular oxygen via two pathways, exchange reaction (I) and the recombination

$$\mathrm{Fe} + \mathrm{O_2} \longrightarrow \mathrm{FeO_2}. \qquad \text{(II)}$$

The rate constants for recombination reaction (II) in the low- and high-pressure limits were obtained within a narrow temperature range around 1150 K [13]. By contrast, the expression for the temperature dependence of the rate constant for exchange reaction (I) could not be previously determined correctly because of the lack of an appropriate program for fitting the experimental data with a nonlinear regression. Therefore, in [12], only a graphical estimate of the rate constant for reaction (I) was derived, which was then presented in [13].

The aim of the present work is to fill this gap and analyze our results on the rate constant of reaction (I) together with the recently reported rate constants for reaction (I) in the forward [14] and reverse (–I) [15] directions with the help of new thermochemical data on the Gibbs energy function [16] and the bond dissociation energy of the FeO molecule [17]. It should be noted that the emergence of new data on the electronic structure of FeO, which underlies calculations of its thermodynamic functions [16], led to a significant change in the value of the Gibbs energy function of this molecule and, consequently, the equilibrium constants for reactions (I) and (–I). An additional motivation for this work was that our graphical evaluation given in [13] was incorrectly digitized and presented in the NIST Chemical Kinetics Database [18] in the form of an Arrhenius dependence that does not correspond to the experimental data presented in [12, 13].

In [12, 13], the rate constant for the interaction of iron atoms with molecular oxygen was determined from the rate of consumption of Fe atoms, which was calculated from the time histories of Fe atom absorption decay. The experiments were performed behind incident shock waves using mixtures containing 6.5 × 10^{-4}% [12] and 3.0 × 10^{-4}% [13] $Fe(CO)_5$ and 0.5%

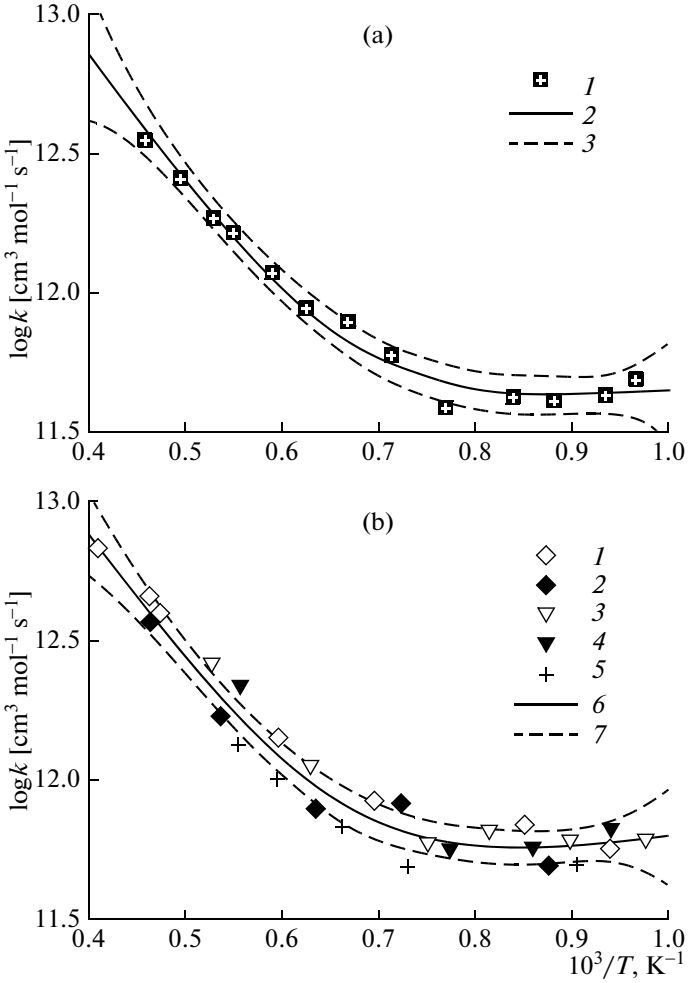

Fig. 1. Temperature dependence of the rate constant for the reaction of Fe atoms with O_2 measured in (a) [12] and (b) [13]. (a) The mixture contained 6.5×10^{-4}% $Fe(CO)_5$ and 0.5% O_2 in Ar: (*1*) experimental values, (*2*) nonlinear regression, and (*3*) respective 95% confidence interval. (b) The mixture contained 3.0×10^{-4}% $Fe(CO)_5$ and various concentrations of O_2 (in %) in Ar or Ar + He: (*1*) 0.33, (*2*) 0.50, (*3*) 1.00, (*4*) 0.33, (*5*) 0.50, (*6*) nonlinear regression, and (*7*) 95% confidence interval. The mixture used in series of experiments (*4*) and (*5*) contained 50% He; in the rest of the cases, the bath-gas was pure argon.

[12] and 0.33–1.0% [13] O_2 in argon and argon + helium over temperature ranges of 1035–2200 K [12] and 1025–2200 K [13] at total gas densities of ~2.5×10^{-6} mol/cm^3 [12] and ~4×10^{-6} mol/cm^3 [13]. The source of Fe-atom resonance radiation ($\lambda = 344.06$ nm) in [12] was an electrodeless bulb lamp fed by a microwave generator at an anode current of 200 mA. In [13], a hollow cathode lamp operating in the pulse mode was used to produce Fe-atom resonance radiation at $\lambda = 371.99$ nm.

The experimental results obtained in [12, 13] are displayed in Figs. 1a and 1b, respectively. The data for plotting the graphs were obtained by processing the original oscillograms. The temperature dependence of the apparent rate constant in the Arrhenius coordinates was approximated by the expression $\log(A\exp(-bx) + Cx^n\exp(-dx))$ ($x = 1000/T$), which shows that exchange reaction (I) is described by the Arrhenius dependence, while recombination reaction (II), by the product of power and exponential functions, where the latter allows for the possible presence of an energy barrier.

Applying nonlinear regression analysis to the data from [12] (Fig. 1a), we obtained the following expression for the temperature dependence of the rate constant for reaction (I):

$$k_1(T) = 6.2\times10^{14}\exp\left(-\frac{11200\text{ K}}{T}\right)\text{cm}^3\text{ mol}^{-1}\text{ s}^{-1}.$$

The expression derived from the data reported in [13] (Fig. 1b) reads as

$$k_1(T) = 6.1\times10^{14}\exp\left(-\frac{11000\text{ K}}{T}\right)\text{cm}^3\text{ mol}^{-1}\text{ s}^{-1}.$$

As can be seen, these expressions are very close in both the preexponential factor and activation energy. Therefore, as the Arrhenius dependence for $k_1(T)$ in

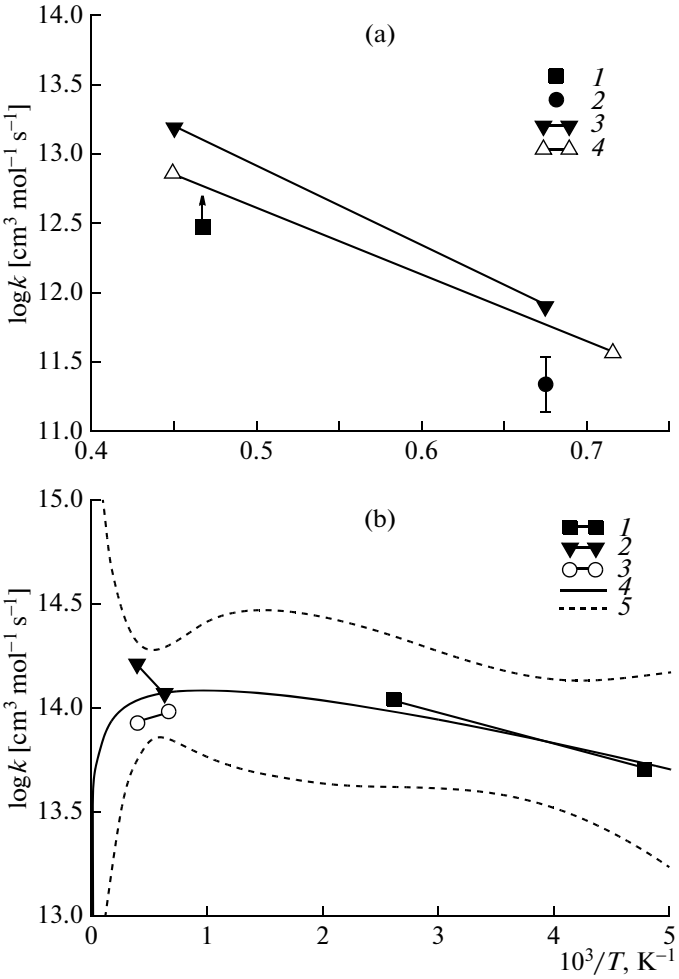

Fig. 2. Comparison of the published rate constants for reactions (a) (I) and (b) (–I). (a) (*1*) [10], (*2*) [11], (*3*) [14], and (*4*) present work. (b) (*1*) Direct measurements [15], (*2*, *3*) calculated based on the rate constants for reaction (I) from (*2*) [14] and (*3*) present work and the equilibrium constant; (*4*) generalized interpolation and (*5*) 95% confidence interval.

the temperature range of 1500–2500 K, we adopted the expression obtained by averaging the parameters of these two expressions:

$$k_1(T) = 6.2\times10^{14}\exp\left(-\frac{11\,100\text{ K}}{T}\right)\text{ cm}^3\text{ mol}^{-1}\text{ s}^{-1}. \quad (1)$$

Figure 2a shows a comparison of our results with the available literature data on $k_1(T)$. As can be seen, the rate constant obtained in the present study is somewhat lower than the results of the recent measurements in shock waves by Roth and coworkers [14], but at the same time, it is markedly higher than the value derived from the flow reactor measurements at 1600 K [11]. The reasons for these discrepancies remain unclear.

The rate constant for the reverse reaction was calculated using the equilibrium constant:

$$k_{-1}(T) = \frac{k_1(T)}{K_{e1}(T)}. \quad (2)$$

The equilibrium constant for reaction (I) was calculated in the standard manner, by the formula

$$K_{e1}(T) = \exp\left(\frac{\Delta_{r1}\Phi^\circ(T)}{R} - \frac{\Delta_{r1}H^\circ(0)}{RT}\right), \quad (3)$$

where $\Delta_{r1}\Phi^\circ(T)$, $\Delta_{r1}H^\circ(0)$ are, respectively, the Gibbs energy function change for the reaction at a temperature T and the enthalpy change at 0 K. The Gibbs energy function change was calculated from the Gibbs energy functions for O, O_2 [19], Fe, and FeO [16]. The enthalpy change was calculated based on the dissociation energy of FeO measured in photodissociation experiments [17]: D_0(Fe–O) = 403.3 ± 1.0 kJ/mol, which is currently considered the most reliable value. A similar value (D_0(Fe–O) = 402 ± 8 kJ/mol) was obtained in [20] based on spectroscopic measurements. Nearly the same value, D_0(Fe–O) = 402.5 ± 12.2 kJ/mol, was derived from mass-spectrometric measurements of equilibria [16]. Since the reaction (I) proceeds through the rupture of the O–O bond and formation of the Fe–O bond, the enthalpy change can

be represented as $\Delta_{r1}H°(0) = D_0(O–O) – D_0(Fe–O) = 493.57 – 403.30 = 90.27$ kJ/mol (the value of $D_0(O–O)$ is taken from [14]).

The temperature dependence of the rate constants for the reverse reaction (–I) calculated by formula (2) from our data and results presented in [14] is shown in Fig. 2b. The results of direct measurements of the rate constant for reaction (–I) at low temperatures (209–381 K) [15] are also presented. Interpolation of the data displayed in Fig. 2b (the value of k_{-1}(1600 K) calculated from k_1(1600) measured in [11] is not included, since it falls out of the main group of measurements) yielded the following expression for $k_{-1}(T)$ in the temperature range of 200–2500 K:

$$k_{-1}(T) = 1.8 \times 10^{14} \left(\frac{1000}{T}\right)^{0.37} \times \exp\left(-\frac{367\ \text{K}}{T}\right) \text{cm}^3\ \text{mol}^{-1}\ \text{s}^{-1}. \quad (4)$$

This result can be explained as follows. With increasing temperature, the inhibitory effect of the energy barrier weakens, but concurrently decreases the cross section of the capture of the O atom by FeO molecule with the formation of the respective transition state [21]. A similar behavior of the temperature dependence of the rate constants was observed for the reaction AlO + O = Al + O_2 [22].

Representing the equilibrium constant $K_{e1}(T)$ in the temperature range 1500–2500 K (the interval in which $k_{e1}(T)$ was measured) as

$$K_{e1}(T) = 5.2\left(\frac{1000}{T}\right)^{-0.392} \exp\left(-\frac{10857K}{T}\right) \quad (5)$$

and substituting $k_{-1}(T)$ and $K_{e1}(T)$ given by (4) and (5) into formula (2), we obtained the following expression for the generalized temperature dependence of the rate constant for reaction (I):

$$k_1(T) = 9.4 \times 10^{14} \left(\frac{T}{1000}\right)^{0.022} \times \exp\left(-\frac{11224\ K}{T}\right) \text{cm}^3\ \text{mol}^{-1}\ \text{s}^{-1}. \quad (6)$$

Thus, in the present work, a correct extraction of the rate constant for reaction (I) from the overall rate constant for reactions (I) and (II) measured in [12, 13] was performed, the rate constant of the reverse reaction (–I) was calculated, and the results obtained were analyzed together with the published data. Based on the available data, generalized expressions for the rate constants of the reaction Fe + O_2 = FeO + O in the forward and reverse direction were derived.

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