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PHYSICAL CHEMISTRY

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1961

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Abstract

Full Text

PHYSICAL CHEMISTRY

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DETERMINATION OF THE RECOMBINATION COEFFICIENT OF OXYGEN ATOMS ON THE SURFACE OF QUARTZ COATED WITH POTASSIUM TETRABORATE

(Presented by Academician V. N. Kondrat' ev on March 30, 1961)

The efficiency of recombination of atoms and radicals on a surface largely determines the influence of the surface on reactions proceeding with the participation of these particles. In particular, the influence of the surface on chain oxidation and combustion reactions is very great. In view of the wide occurrence of chain oxidation reactions involving hydrogen atoms, oxygen atoms, and OH radicals, especially many works have been devoted to determining their recombination coefficients on various surfaces. In almost all works the probe method was used (¹⁻⁵). This method has the disadvantage that near the probe a considerable concentration gradient of the recombining particles is created (especially at high recombination efficiencies), which introduces a significant error into the measurement results. The use of Wrede-Harteck manometers to eliminate this drawback (⁶) is associated with a complication of the procedure.

To determine the recombination coefficient of oxygen atoms on quartz, K. H. Krongelb and M. W. P. Strandberg (⁷) used the electron paramagnetic resonance method. However, the measurements were carried out at room temperature. Determination by this method at the temperatures of oxidation and combustion reactions leads to great experimental difficulties.

For determining the recombination coefficient of hydrogen atoms (ε_{H}) on various surfaces, a method based on measuring the first ignition limit of mixtures of hydrogen with oxygen in vessels coated with the substance under investigation, as well as a method based on measuring the shift of this limit upon introducing into the vessel rods with the corresponding coating, has proved very fruitful (^{8,9}). These methods have the advantage that they do not require knowledge of the concentrations of the recombining particles, are simple, and make it possible to determine ε_{H} at the temperatures at which combustion processes occur.

However, determination of ε_{H} from the first ignition limit of a hydrogen-oxygen mixture is possible because in such a system the concentration of H atoms greatly exceeds the concentration of O atoms and OH radicals, and, consequently, the

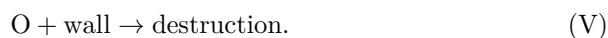
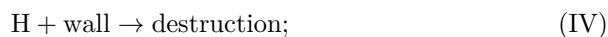
Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

position of the limit is determined by the competition between the reaction of H atoms in the volume, leading to chain branching, and their heterogeneous recombination.

To study the efficiency of heterogeneous recombination of oxygen atoms (ε_O) by the method of measuring ignition limits, it is necessary to choose a system in which the concentration of O atoms would be at least comparable with the concentration of hydrogen atoms, i.e., a system in which the chain-branching process would depend on the rate of reactions of atomic oxygen. Such a system, with a well-known reaction mechanism, is the low-temperature combustion of carbon monoxide in the presence of small additions of hydrogen (¹⁰⁻¹²).

The mechanism of this reaction near the first ignition limit may be represented by the following scheme:



On the basis of this scheme, from the critical condition for self-ignition ¹³ it is easy to obtain the expression

$$(\text{O}_2)^{\text{CO}} = \frac{(k_4)^{\text{CO}}}{2k_2} \left[1 + \frac{(k_5)^{\text{CO}}}{k_3(\text{H}_2)} \right], \quad (1)$$

Fig. 1. Dependence of the ignition limits on temperature for mixtures $2\text{H}_2 + \text{O}_2$ (1) and $2\text{CO} + \text{O}_2 + x\text{H}_2$ (2, 3, 4): 2- $x = 6.0\%$; 3- 4.0% ; 4- 1.95% .

Fig. 2. Dependence of $p_{\text{O}_2}^{\text{CO}}$ on $1/p_{\text{H}_2}^{\text{CO}}$ at temperatures: 1- 550° ; 2- 575° ; 3- 600° ; 4- 620° ; 5- 640° .

where $(\text{O}_2)^{\text{CO}}$ and $(\text{H}_2)^{\text{CO}}$ are the concentrations of oxygen and hydrogen at the first ignition limit; k_i are the rate constants of the corresponding reactions. The superscripts indicate that the quantities refer to mixtures of CO with O_2 containing small additions of H_2 .

In the case where the reactions of heterogeneous chain termination proceed in the kinetic region, k_4 and k_5 do not depend on the composition of the mixture. Therefore, omitting the superscripts on these constants and replacing the concentrations in (1) by partial pressures, we obtain:

$$p_{\text{O}_2}^{\text{CO}} = \frac{k_4 T}{2k_2 \cdot 10^{19}} \left(1 + \frac{k_5 T}{k_3 \cdot 10^{19} \cdot p_{\text{H}_2}^{\text{CO}}} \right). \quad (2)$$

It follows from this expression that, when reactions (IV) and (V) proceed in the kinetic region, the dependence of $p_{\text{O}_2}^{\text{CO}}$ on $1/p_{\text{H}_2}^{\text{CO}}$ at constant temperature must be linear, with the intercept on the ordinate axis equal to

$$b = \frac{k_4 T}{2k_2 \cdot 10^{19}}, \quad (3)$$

and with the slope equal to

$$\text{tg } \alpha = \frac{k_4 T}{2k_2 \cdot 10^{19}} \frac{k_5 T}{k_3 \cdot 10^{19}} k_3. \quad (4)$$

Thus, by measuring at different temperatures the first ignition limits of mixtures of CO and O_2 containing various small additions of hydrogen, one can find $\text{tg } \alpha$ and b and, using the known value of k_3 , determine k_5 .

The recombination coefficient (ε_0) of O atoms (ε_0) can be found from the value of k_5 by the expression:

$$k_5 = \frac{\varepsilon_0 v_0}{d}, \quad (5)$$

where v_0 is the thermal velocity of O atoms; d is the vessel diameter ⁽⁸⁾.

If, in the temperature interval studied,

$$\varepsilon_0 = \varepsilon_0^0 e^{-E_5/RT},$$

then from (3) and (4), and from the temperature dependence of v_0 , it is easy to obtain the equation

$$\lg \frac{\text{tg } \alpha}{bT^{1.5}} = \lg \frac{k_5^0}{k_3^0 \cdot 10^{19}} + \frac{E_3 - E_5}{2.3RT}, \quad (6)$$

Fig. 3. Dependence of $\lg \frac{\operatorname{tg} \alpha}{bT^{1.5}}$ on $1/T$

Figure 2: Fig. 3. Dependence of $\lg \frac{\operatorname{tg} \alpha}{bT^{1.5}}$ on $1/T$

where

$$k_5^0 = \frac{\varepsilon_0^0 \sqrt{8R/\pi m_0}}{d}. \quad (7)$$

According to (6), in this case a linear dependence should be observed between $\lg \frac{\operatorname{tg} \alpha}{bT^{1.5}}$ and $1/T$.

From the slope of the straight line and from the known value of E_3 , one can determine E_5 , and from the intercept, equal to $\lg \frac{k_5^0}{k_3^0 \cdot 10^{19}}$, one can calculate ε_0^0 .

The experiments were carried out in a quartz vessel coated with potassium tetraborate, 2.8 cm in diameter and 14 cm long. Before the measurements, the surface was treated by repeated ignitions of a hydrogen-oxygen mixture, as a result of which the limit decreased to a certain stable value. The procedure for carrying out the experiments was described earlier ⁽¹⁴⁾.

The ignition limits were measured in the temperature interval 550–640° for mixtures 2CO + O₂ containing 1.95, 4.0, and 6.0% H₂, and for the mixture 2H₂ + O₂. The results of these measurements are presented in Fig. 1. The ignition limits obtained are more than 100 times lower than the corresponding limits in a vessel coated with MgO, which ensures the course of reactions (IV) and (V) in the diffusion region ⁽¹⁵⁾.

Fig. 3. Dependence of $\lg \frac{\operatorname{tg} \alpha}{bT^{1.5}}$ on $1/T$

The low ignition limits of mixtures of H₂ with O₂ and CO with O₂, as well as the dependence of the values of the limits on the state of the surface, indicate that reactions (IV) and (V) proceed in the kinetic region.

Taking into account that

$$\frac{k_4}{2k_2} = [\text{O}_2]_{\text{H}_2},$$

where $[\text{O}_2]_{\text{H}_2}$ is the oxygen concentration at the first ignition limit of the hydrogen-oxygen mixture, the right-hand side of expression (3) can be replaced by $p_{\text{O}_2}^{\text{H}_2}$. This means that the intercept on the ordinate axis of the straight line

$p_{\text{O}_2}^{\text{CO}} - 1/p_{\text{H}_2}^{\text{CO}}$ is equal to the partial pressure of oxygen at the first ignition limit of the mixture H_2 with O_2 .

The dependence of $p_{\text{O}_2}^{\text{CO}}$ on $1/p_{\text{H}_2}^{\text{CO}}$ at various temperatures is presented in Fig. 2. As is seen from the figure, the experimental data confirm

the validity of equation (1). With the aid of these straight lines, $\text{tg } \alpha$ and b were calculated. The dependence of $\lg \frac{\text{tg } \alpha}{bT^{1.5}}$ on $1/T$ is presented in Fig. 3. The quantity $E_3 - E_5$, calculated from the slope of the straight line according to (6), proved to be equal to 5.6 ± 0.2 kcal/mole. Taking into account that $E_3 = 11.7 \pm 0.7$ kcal/mole, we obtain ⁽¹⁵⁾ $E_5 = 6.1 \pm 1.0$ kcal/mole. ε_0 , calculated from (6) and (7) from the intercept on the ordinate axis and from the value $k_3 = 1.1 \cdot 10^{-10} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{sec}^{-1}$, proved to be equal to $1.65 \cdot 10^{-2} \text{ sec}^{-1}$.

Thus, in the temperature interval studied, ε_O can be represented in the form

$$\varepsilon_O = 1.65 \cdot 10^{-2} e^{-(6100 \pm 1000)/RT} \text{ sec}^{-1}.$$

From the values of b found graphically and the known value of k_2 ⁽¹⁵⁾, according to equation (4) and an expression analogous to (5), the recombination coefficient of hydrogen atoms on the wall (ε_H) was calculated for various temperatures; it proved to be equal to

$$\varepsilon_H = 9 \cdot 10^{-14} e^{-(5400 \pm 1000)/RT}.$$

The values of ε_H determined by us are in good agreement with the values obtained by A. B. Nalbandyan and S. M. Shubina ⁽⁹⁾ and by N. N. Semenov ⁽¹⁶⁾.

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Received
25 III 1961

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