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Abstract

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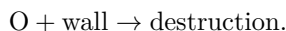
Physical Chemistry

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DETECTION OF OXYGEN ATOMS IN A RAREFIED FLAME OF CARBON MONOXIDE WITH OXYGEN IN THE PRESENCE OF SMALL ADDITIONS OF HYDROGEN

(Presented by Academician V. N. Kondrat'ev, 31 V 1961)

Low-temperature combustion of carbon monoxide, catalyzed by small additions of molecular hydrogen, near the first limit of self-ignition is explained by the following set of elementary reactions (¹⁻⁴):



It follows from the chain mechanism of the reaction that very large concentrations of hydrogen and oxygen atoms and hydroxyl radicals, greatly exceeding the equilibrium concentrations, must be formed in the combustion zone. From the scheme given, taking into account the rate constants of the elementary reactions (⁴⁻⁶), it also follows that in flames of these mixtures the concentrations of hydrogen and oxygen atoms must be comparable and must greatly exceed the concentration of OH radicals.

In flames of moist mixtures of CO with O₂, where the catalytic action of water is analogous to that of hydrogen (²), V. N. Kondrat'ev did in fact detect superequilibrium concentrations of hydroxyl (²). By the thermoelectric-probe method (⁷) it was established that in the flame of these mixtures there are large concentrations of active particles recombining on the specially treated surface of the probe. Taking into account that the concentration of the hydroxyl radical is much lower than the concentration of H and O atoms and that the diffusion coefficient of O is smaller than the diffusion coefficient of H, the authors consider the recombining particles to be H atoms.

Until recently there had been no direct experiments on the immediate detection of H and O atoms and measurement of their concentration in flames of CO with O₂ with small additions of H₂. Recently we succeeded in detecting hydrogen

Fig. 1

Figure 1: Fig. 1

atoms in these mixtures by the EPR method, in concentrations several orders of magnitude higher than equilibrium ⁽⁸⁾.

The present work is devoted to the detection of O atoms in a rarefied flame of mixtures of CO with O₂ containing small additions of molecular hydrogen. For this purpose we used the EPR method. The experimental procedure is described in the work of V. N. Panfilov, Yu. D. Tsvetkov, and V. V. Voevodskii ⁽⁹⁾. To obtain the lowest possible efficiency of recombination of atoms on the surface, the reaction tube was washed successively with hydrofluoric acid and distilled water and coated with potassium tetraborate. Then, for several days, the tube was treated with a stationary flame in a jet of a mixture of CO with O₂ containing additions of H₂. Such treatment made it possible to obtain flames of these mixtures at pressures not exceeding 1.5–2 mm Hg in the temperature interval 600–650°.

The experiments were carried out with a stoichiometric mixture of CO with O₂ containing up to 7% H₂, at a volumetric jet velocity equal to 82 cm³/min (linear velocity 18 m/sec) and at a mixture pressure equal to 5.5 mm Hg. The temperature was varied from 607 to 650°.

Under these conditions an EPR signal of atomic oxygen was recorded, with a *g*-factor equal to 1.5, consisting of one component.

Figure 1 shows the spectrum of atomic oxygen obtained for a mixture containing 2.7% hydrogen at 645°. The value of the *g*-factor obtained by us coincides with the value known in the literature for atomic oxygen obtained in a discharge ^(10–12). As was shown by Ultee ⁽¹²⁾, the form of the spectrum depends substantially on the pressure, and at pressures exceeding 0.2 mm Hg the four components due to the ³P₂ state merge into one line.

Fig. 1

Along with determination of the concentrations of O atoms, parallel measurements of the concentrations of H atoms were carried out.

The dependence of the concentrations of H and O atoms on the content of H₂ in a stoichiometric mixture of CO with O₂ at 610° was studied. From the measurement results presented in Table 1, it follows that the concentrations of O atoms are indeed comparable with the concentrations of H atoms and that both of these concentrations increase with increasing H₂ content in the mixture. The ratio (O)/(H), however, decreases from 4.5 to 0.9 as the H₂ content increases from 1.1 to 6.9%.

With an increase in temperature from 607 to 650° in a mixture containing 3.8% H₂, the concentrations of H and O atoms increase from $2.9 \cdot 10^{14}$ to $4.1 \cdot 10^{14}$

particles/cm³ and from $4.6 \cdot 10^{14}$ to $7.8 \cdot 10^{14}$ particles/cm³, respectively.

Table 1

H ₂ content in the mixture, %	[H] · 10 ⁻¹⁴ , particles/cm ³	[O] · 10 ⁻¹⁴ , particles/cm ³	[O]/H
1.1	0.3	1.5	4.5
1.7	1.3	4.1	3.2
2.4	2.1	5.9	2.8
2.7	2.4	6.4	2.7
3.1	3.4	5.9	1.7
4.4	4.1	6.0	1.4
5.1	5.2	5.9	1.1
6.1	5.6	6.0	1.1
6.9	6.8	6.4	0.9

From the obtained values of the concentrations of H and O atoms, it follows that their total partial pressure reaches 2% of the total pressure.

It should be noted that the very high concentrations of oxygen and hydrogen atoms found by us still do not fully reflect the true concentrations of these particles in the flame, where, evidently, their concentration is still higher. The method used by us makes it possible to measure the concentration of atoms not in the flame itself, but at a distance of about 10 mm from it.

The detailed studies we have undertaken of the dependence of the concentrations of O and H on various parameters will make it possible in the future to approach a more accurate determination of the relation between the concentrations measured by us and those present in the flame itself. This will also make it possible to come closer to a more complete elucidation of the mechanism of CO oxidation.

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