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Abstract

Full Text

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ON THE EXISTENCE OF THE HIGHER OXIDE CO_3

(Presented by Academician V. N. Kondrat' ev, 17 V 1957)

The results of a study of the percentage combustion of a mixture of CO and O_2 as a function of the water-vapor content lead to the conclusion ([1]) that in dry mixtures the reaction rate must be equal to zero. However, Lewis and Elbe ([2]) consider it possible for the reaction between CO and O_2 to proceed without the presence of water vapor; oxidation in this case is accompanied by the participation of the hypothetical higher oxide CO_3. It is assumed that the structure of this oxide has the form:

$$O = C\begin{matrix}/O \\ \backslash O\end{matrix}$$

From experimental data it is known that the bands in the infrared absorption spectra of CO_2, C_3O_2, HCOOH, etc., corresponding to valence vibrations of C=O, are very intense ([3]), and from these bands very small concentrations of impurities of the indicated gases can be detected. Consequently, the higher oxide CO_3, if it really exists, should be detected by the infrared radiation of a diffusion flame of CO in O_2. The possible value of the frequency corresponding to vibrations of the C=O bond can be roughly estimated from the condition of equality of the force constants for this bond in the molecules CO_3 and HCOOH and is approximately 1660 cm^{-1}.

Fig. 1. Burner diagram

Fig. 3 and Fig. 4

Figure 3: Fig. 3 and Fig. 4

Fig. 2. Portion of the spectrum of a CO flame with a band $\nu = 1615$ cm^{-1}: *I* –10 mm from the burner; *II* –1.5 mm from the burner

In order to detect the higher oxide CO_3, we used an IKS-11 infrared spectrometer. To increase the intensity of the radiation incident on the entrance slit, a spherical mirror was placed behind the flame at a distance equal to the radius of curvature. Carbon monoxide was obtained by the action

sulfuric acid by heating the latter, washed with a solution of NaOH, and collected over water in a gasometer made of galvanized or ungalvanized sheet iron. Before combustion, the gas was carefully dried by passing it through special dryers with P_2O_5. Technical oxygen was used as the oxidant. In those cases where isolation of the flame from atmospheric moisture was required, the burner was blown with dried nitrogen, and to isolate the flame from nitrogen and moisture –with oxygen. Oxygen and nitrogen were also passed through special dryers with P_2O_5. The form of the burner is shown schematically in Fig. 1.

The frequencies were measured by a high-precision graphical method ([4]).

We do not give here a complete description of the emission spectrum of the diffusion flame of CO in O_2, but confine ourselves only to indicating that, in the frequency interval from 6000 to 400 cm^{-1}, it contains up to 100 lines and bands due to the radiation of CO, OH, CO_2, HO_2, and H_2O. In the spectrum of the flame, when CO, O_2, and N_2 have been thoroughly dried, only the bands and lines of CO and CO_2 appear. If, however, the image of

Fig. 3

Fig. 4

Fig. 3. Graph of the dependence of the intensity of the band $\nu = 1615$ cm^{-1} on the content of O_2 in the mixture
$O_2 + N_2$

Fig. 2. Graph of the dependence of the intensity of the bands in the spectrum on height. The intensity of the OH line was estimated by eye

the base of the flame (not higher than 3.5 mm from the burner, with a total height of the visible cone of 15-17 mm) is directed onto the spectrometer slit, a band appears in the spectrum with a frequency of maximum intensity at $\nu = 1615$ cm^{-1}, which is not due to the radiation of the particles listed above (Fig. 2). At first we were inclined to identify this band with the NO_2 band (in absorption $\nu = 1621$ cm^{-1}). However, if the flame is isolated from access of atmospheric nitrogen by blowing with dried oxygen, this band not only does not disappear but even becomes several times more intense. An increase in intensity is also observed if the oxygen concentration in the oxidizing mixture of O_2 and

N_2 is varied. The curve of the dependence "radiation intensity in arbitrary units—amount of oxygen in a given volume of the oxidizing mixture" is shown in Fig. 3. In these experiments it was easy to detect, by smell, the presence of ozone in the combustion products. Next, the dependence of the intensity of the band $\nu = 1615$ cm^{-1} on the humidity of CO was investigated. The experiments showed that increasing the humidity of CO does not lead to a noticeable change in the intensity of the indicated band. Therefore, further investigations were continued without drying the gases used. In particular, the dependence of the intensity of the OH, CO, CO_2, H_2O bands and $\nu = 1615$ cm^{-1} in different regions of the flame along its height was studied. From the curves obtained it is clear (Fig. 4) that the band $\nu = 1615$ cm^{-1} has maximum intensity at the very base of the ···

flame base; as its height increases, its intensity falls off very rapidly, and at a height of 3.5 mm it is already equal to zero.

The maxima of the intensities of the CO and OH bands are shifted somewhat upward, still higher than the maximum intensity of the CO_2 bands, and, finally, in the middle of the height of the visible cone of the flame the H_2O bands reach their maximum intensity.

On the basis of an analysis of the experimental data obtained, we came to the conclusion that the carrier of the band $\nu = 1615$ cm^{-1} is the higher oxide CO_3. In the spectrum, apparently, only the *Q*-branch of the band appears most distinctly, while the *P*- and *R*-branches are superposed on the bands of CO_2 and H_2O, and their observation is difficult. If this is so, then the short-wavelength boundary gives the frequency $\nu = 1655$ cm^{-1}, which is very close to the calculated frequency 1660 cm^{-1} given by us above. Our conclusion is further confirmed by the fact that Knipe and Gardon ([5]) also indicate the possibility of the existence of CO_3 on the basis of a study of the electronic radiation of a CO and O_2 flame. However, the absence of an influence on the intensity of the band from the presence of water vapor in the combustion zone remains unclear.

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