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ON THE INFLUENCE OF IMPURITIES ON THE EXCITATION OF VIBRATIONS OF OXYGEN MOLECULES AT HIGH TEMPERATURES

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The process of excitation of molecular vibrations is being studied by many investigators, using a wide variety of methods and under different conditions. It was noted long ago that the relaxation time of molecular vibrations depends strongly on the degree of purity of the gas, i.e., on the presence in the gas of appreciable amounts of impurities, especially at low temperatures. Investigations carried out (1,2) in oxygen with a small impurity content at room temperatures showed that the excitation time of vibrations of O_2 molecules decreases greatly with increasing impurity concentration. It was also expected that, with rising temperature, the influence of impurities would become insignificant. This was shown experimentally for dried and undried air in (3) at temperatures close to 2000° K, when the effect of water vapor on the relaxation time of O_2 molecules decreased so much that it could be neglected. Relying on the result obtained, the author of (3) considered it possible to work with oxygen containing appreciable amounts of impurities at lower temperatures, down to $T = 760°$ K. The results obtained appeared so well founded that they served as a criterion for testing the Landau–Teller theory, and attempts were also made on their basis to calculate the force constants of the O_2—O_2 interaction potential (4,5). It turned out that the data of (3) do not, over the entire range of the investigation, follow the temperature dependence predicted by the theory. Therefore either the theory of excitation of molecular vibrations in this temperature range is incorrect, or the experimental data are erroneous, and, consequently, the force constants calculated on the basis of the Landau–Teller theory and the experimental data of work (3) also cannot be correct.

Therefore, in the present work an attempt was made to check the results of (3), and also to study the influence of some of the most effective impurities on the rate of excitation of vibrations of O_2 molecules over a wide temperature interval

Fig. 1. Plot of the dependence $\log\{\tau(1-e^{-\theta/T})\}$ on $T^{-1/3}$, where a—results of the present work, b—results of paper (6), c—results of paper (3).

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from 1200 to 6600° K. For this purpose the previously described apparatus (6) was used without substantial changes, except for the part related to measuring the shock-wave velocity: ionization probes were replaced by piezoelectric probes.

Since special attention was paid to the effect of impurities on the excitation time of vibrations of O_2 molecules, the oxygen taken from standard cylinders was carefully purified of possible impurities by repeated fractionation. For this purpose it was passed through a column with silica gel and then liquefied in a coil immersed in liquid nitrogen, and was partly pumped off together with the impurities that had not frozen out (nitrogen, etc.). Next, the oxygen was slowly evaporated into an evacuated vessel, and the remaining part together with the frozen impurities was removed. This procedure was repeated twice. Mass-spectrometric analysis of the oxygen purified in this way showed the presence of only 0.8% argon; the remaining impurities amounted to substantially less than 0.01%.*

The shock tube, evacuated to an initial pressure of $2 \cdot 10^{-2}$ mm Hg, was filled several times before the experiment with oxygen to a pressure of 50 mm Hg and evacuated again; after that the required initial pressure was set, which was varied from 1 to 250 mm.

Helium at a pressure of 50-90 atm and hydrogen at a pressure of 10-25 atm were used as the driver gas; shock-wave velocities in the range 1.3-3 km/sec were obtained. The error in the experimental measurement of the velocity was 1-2%. The method used by us made it possible to obtain the distribution of the absorptivity of vibrationally excited oxygen behind the shock-wave front. The form of these oscillograms, as well as the method for calculating the values of the relaxation time of vibrations of O_2 molecules, are described in paper (6). As before, no difference in the results was observed when the driver gas helium was replaced by hydrogen.

Three series of experiments were carried out: 1) with purified oxygen; 2) with oxygen passed through a silica-gel column and not subjected to fractionation; 3) to study the process of excitation of vibrations of O_2 molecules upon addition to the purified gas of 1% CO_2, 0.53% H_2O, 1% H_2O, 1% NO_2, 0.25% C_2H_5OH, 0.5% C_2H_5OH.

Fig. 1. Plot of the dependence $\log\{\tau(1-e^{-\theta/T})\}$ on $T^{-1/3}$, where a—results of the present work, b—results of paper (6), c—results of paper (3).

* The author expresses gratitude to A. V. Bondarenko for carrying out the mass-spectrometric analysis of the gas investigated.

The results of the first series of experiments, together with the data of paper (6) up to a temperature of 7000°K and of papers (3), are presented in Fig. 1, where the quantity $T^{-1/3}$ is plotted along the abscissa, and along the ordinate $\lg\tau\cdot(1-e^{-\theta/T})$, where τ is the relaxation time of O_2, reduced to one atmosphere; θ is the characteristic vibrational temperature of O_2; T is the gas temperature. It should be noted that these values agree well at temperatures above 2000°K. However, in the low-temperature region, beginning approximately at 2000°K, the results of the present work differ from Bleakman' s results, the discrepancy increasing with decreasing temperature and at 1200°K reaching more than 100%. The relaxation times obtained in (3) are substantially shorter than the values obtained in the present work. This is apparently connected either with the presence of impurities in the gas under study itself, which was not purified sufficiently thoroughly, or with the presence of impurities in the shock tube, which was evacuated only to 0.5 mm and, moreover, was not "flushed" with the gas under study. Among the possible highly effective impurities, in addition to water vapor, one should include helium, which could have remained in the apparatus as a result of insufficient evacuation.

The results of the present work and of paper (6) follow very well the temperature dependence of the Landau-Teller theory, i.e., over a wide temperature interval all the experimental values, to within the errors of the experiment, lie on a single straight line.

Figure 2 gives the relaxation times in impure oxygen taken from standard cylinders. Mass analysis for such oxygen gives the following impurity composition: 2% N_2, 0.5% CO_2, and 0.05% H_2O. On the same figure, for comparison, are plotted the values of the relaxation time for puri-

purified oxygen O_2. It is not difficult to notice a substantial difference between the results of the two series of experiments; the excitation times of vibrations of O_2 molecules in unpurified oxygen are noticeably shorter in the temperature interval $T < 3000$°K, and this difference increases as the temperature is lowered. Thus, for example, at 4000°K one may consider that these times practically coincide within the experimental error, whereas at 1500°K they differ by a factor of 2.

In Fig. 3 the results of the third series of experiments are presented. First of all, the influence of water vapor on the relaxation time of O_2 was subjected to detailed study. It is known that water vapor is extremely effective in exciting vibrations of O_2 molecules at room temperatures. This is associated with the phenomenon of resonance, since one of these frequencies of the water molecule practically coincides with the vibrational frequency of O_2. Since the excitation time of vibrations of H_2O in its own gas even at room temperature is of the order of $2\cdot10^{-8}$ sec, and the probability of exchange of vibrational quanta under resonance is extremely large in comparison with the probability of exchange between translational and vibrational degrees of freedom, a continuous transfer of vibrational quanta from H_2O molecules to O_2 takes place, which greatly reduces the relaxation time of O_2 even at sufficiently high temperatures.

Figure 2. Graph of the dependence of the excitation time of vibrations of O_2 molecules in a medium of frozen (a) and unfrozen (b) oxygen

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The influence of water vapor on the establishment of equilibrium over the vibrational degrees of freedom was investigated in the temperature interval 1350—5500°K. It turns out that at $T = 1500$°K, 0.53% H_2O can reduce τ_{eff} by half, i.e., water vapor at this temperature is more than two orders of magnitude more effective than O_2 molecules in exciting O_2 vibrations, while in the region $T = 3000$°K the addition of 0.53% water vapor has no noticeable influence on the relaxation of O_2, since at this temperature excitation of O_2 occurs mainly through O_2—O_2 collisions.

At higher temperatures for the mixture indicated above, and also for a mixture 99% O_2+1% H_2O, τ_{eff} increases in comparison with τ_{O_2}, and for $T = 4250$°K the addition of 1% H_2O to oxygen causes an increase of τ_{eff} by 55%. An analogous phenomenon is also observed for the mixture $99\% O_2 + 1\% CO_2$ at temperatures above 3000°K. Here it is expressed still more strongly: at $T = 4250$°K the addition of 1% CO_2 increases τ_{eff} by 75%. Below $T = 3000$°K, such an amount of CO_2 impurity produces no noticeable effect on the relaxation in oxygen.

Of all the impurities investigated in the present work, the impurity of ethyl-alcohol vapor proved to be the most effective. At a temperature $T = 2250$°K the alcohol vapor is four times more effective than water vapor. Above the temperature $T = 4000$°K, the influence of an impurity of 0.25 and 0.5% C_2H_5OH does not affect the process of vibrational excitation near the front of the shock wave. However, with distance from it, dissociation of C_2H_5OH occurs and the effect of an increase of τ_{eff} over the relaxation zone of O_2 is observed. Such an increase of τ also takes place in the case of pure O_2, but for a mixture of oxygen and alcohol this tendency is expressed much more strongly, as is seen in Fig. 3, where in the temperature intervals

4300–4500° K and 5250–5500° K; along the ordinate axis are plotted τ, calculated over the entire relaxation zone for two different shock-wave velocity values.

The effect of a 1% $\mathrm{NO_2}$ impurity on the excitation time of $\mathrm{O_2}$ was studied in the range $T = 2400$–6000° K. The results of this study show that at $T = 2400$° K, τ_{eff} is half as long as $\tau_{\mathrm{O_2}}$. As the temperature increases, the difference

Fig. 3. Dependence of the time of excitation of vibrations of $\mathrm{O_2}$ molecules in

a medium of frozen oxygen (solid line) and in mixtures: 99% O_2 + 1% CO_2 (a); 99.47% O_2 + 0.53% H_2O (b); 99% O_2 + 1% H_2O (c); 99% O_2 + 1% NO_2 (d); 99.75% O_2 + 0.25% C_2H_5OH (e); 99.5% O_2 + 0.5% C_2H_5OH (e)

between these relaxation times decreases and, beginning at approximately $T =$ 4000° K, the influence of this amount of NO_2 on the time of excitation of vibrations of O_2 molecules becomes insignificant.

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