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Fig. 1

Figure 1: Fig. 1

Abstract

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STUDY OF THE DECOMPOSITION OF CARBON DIOXIDE MOLECULES AT HIGH TEMPERATURES

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The study of physicochemical processes occurring in gases at temperatures of several thousand degrees is now being carried out on a fairly broad front; however, the literature contains no data on the rate of decomposition of carbon dioxide molecules, despite the great interest in the kinetics of phenomena in which carbon dioxide participates. Relying on a previously developed method for measuring the rate of decomposition of molecules at high temperature, developing behind the front of a strong shock wave (1-3), in the present work an attempt has been made to obtain information on the course of the dissociation process of carbon dioxide molecules.

In the experiments, the distribution of the absorptivity of heated carbon dioxide behind the front of a shock wave propagating in a shock tube was measured. Absorption of ultraviolet radiation was studied in the wavelength region $\lambda = 2380$ Å and $\lambda = 3000$ Å. Since earlier no reliable absorption of light by heated carbon dioxide had been observed in this spectral region, in order to determine the origin of the observed absorption special experiments were carried out with carbon monoxide and oxygen, with the aim of clarifying the possible contribution to the absorption of these gases as products of CO_2 decomposition. It turned out that neither these gases nor other possible impurities could make a noticeable contribution to the observed absorption*. It may be assumed that this absorption is due to broadening of the continuum determined by the transition $1\pi_g \rightarrow 3\sigma_u$ (5), as a consequence of transitions from excited vibrational levels of the ground electronic state of the CO_2 molecule.

Fig. 1. Oscillogram of the distribution of absorptivity ($\lambda = 3000$ Å) behind the front of a shock wave propagating in carbon dioxide at a speed of 3.25 km/sec at an initial pressure of 5.3 mm Hg. Below is the zero line. Time marks are at intervals of 1 μsec.

The observed oscillograms of the distribution of absorptivity behind the shock-wave front had the form shown in Fig. 1. It was assumed that excitation of the vibrations of CO_2 molecules occurs considerably faster than decomposition, so that the rise of absorption in the wave front is associated with excitation of the vibrations of CO_2 molecules, while the observed decrease in absorption is associated with decomposition of CO_2 molecules. The basis for this assumption was the smallness of the vibrational relaxation time measured in a number of works (6-8). This makes it possible, on the basis of the laws of conservation of mass, momentum, and energy and the equation of state, to calculate the values of all gas characteristics in the region of maximum absorption from the measured initial gas pressure and shock-wave velocity. Carrying out experiments over a wide range of values of the gas parameters behind the wave front (temperature

* The possibility of the appearance of appreciable absorption in heated CO_2 was predicted by Gaydon (4).

$1300 \leq T \leq 6300°K$, pressure $0.16 \leq p \leq 2.72$ atm, concentration of CO_2 molecules $2.2 \cdot 10^{17} \leq n_{CO_2} \leq 3.2 \cdot 10^{18}$ cm^{-3}), we determined the dependence of the absorptivity A on the temperature T and the concentration n_{CO_2} in the form of Beer' s law $A = 1 - \exp(-\sigma n_{CO_2} l)$, where σ is the absorption cross section, which depends on temperature, and l is the path length in the absorbing gas.

Fig. 2. Dependence of the rate of decomposition of carbon dioxide molecules $W = (d\xi_{CO_2}/dt)$ on the concentration of CO_2 molecules at temperature $T = 4000°K$

We shall determine the rate of decomposition of carbon dioxide molecules at the very beginning of the decomposition zone, in the region of maximum absorption, when it may be assumed that the CO_2 molecules decompose into CO and O, and that the O atoms do not have time to recombine into O_2 molecules (since recombination proceeds through triple collisions O + O + M). Let us suppose that the reaction $CO_2 + O \rightarrow CO + O_2$ can become significant only at later stages in the development of the process of carbon dioxide decomposition. Naturally, the assumptions made are not fully justified, since so far we have not been able to follow simultaneously the change in the concentrations of the two gas components behind the wave front in CO_2.

Differentiating the expression of Beer's law, for the point m of maximum absorption we obtain a relation between the derivative of the absorptivity $(dA/dt)_m$ and the gradients of concentration $(dn_{CO_2}/dt)_m$ and temperature $(dT/dt)_m$. To eliminate $(dT/dt)_m$ we use the expression of the law of conservation of energy. The concentrations of CO and O entering into this expression are eliminated by means of relations following from the law that the sum of the partial pressures of the components of a mixture of ideal gases is equal to the total pressure, and from the condition that the ratio of the total number of carbon atoms to the total number of oxygen atoms is constant. Thus, for the rate of change of the mole fraction of CO_2 molecules, $\xi_{CO_2} = n_{CO_2}(kT/p)$, at the very beginning of the decomposition zone ($\xi_{CO_2} = 1$), we obtain

Fig. 3. Values of the rate constant for bimolecular decomposition of CO_2 molecules

$$\frac{d\xi_{CO_2}}{dt} = \frac{kT}{pl\bar{\rho}} \frac{\dfrac{1}{1-A}\left(\dfrac{dA}{dt}\right)_m}{\sigma + \left[\left(\dfrac{d\sigma}{dT} - \dfrac{\sigma}{T}\right)\dfrac{C + h_{CO} + h_O - 2h_{CO_2}}{2\dfrac{dh_{CO_2}}{dT}}\right]},$$

where $C = (\mu V^2/2)\,[1-(1/\bar{\rho})^2]+h^0_{CO_2}$, h is the value of the molar enthalpy of the corresponding components (with allowance for the expenditure on dissociation), h^0 is the value of h before the wave front, V is the wave velocity, $\bar{\rho}$ is the ratio of the density values at the wave front, p is the pressure behind the front, μ is the molecular weight of carbon dioxide, and k is Boltzmann' s constant. In deriving this relation it was assumed that the pressure p in this region remains constant.

The results of the experiments carried out are presented in Figs. 2-4. The obtained dependence $W = (d\xi_{CO_2}/dt)$ on the concentration of CO_2 molecules n_{CO_2} (Fig. 2), despite the considerable scatter of the results associated with inaccu-

···characteristics of the measured value $(dA/dt)_m$, indicates that the decomposition of CO_2 molecules proceeds by way of a bimolecular reaction. Then, for the reaction $CO_2 + CO_2 \rightarrow CO + O + CO_2$, neglecting at the very initial stage of decomposition the possible influence of recombination, one can obtain values of the rate constant of decomposition k_{CO_2} of CO_2 molecules. For conditions in the flow behind the shock-wave front,

$$W = -(1 + \xi_{CO_2})\, k_{CO_2} \xi^2_{CO_2}\, (p/kT);$$

putting $\xi_{CO_2} = 1$, from this we find the values k_{CO_2} (Fig. 3). It was possible to measure values of k_{CO_2} for temperatures from 3000 to 5500° K; at $T < 3000°$ the decomposition process proceeds so slowly that, from the slope of the absorption curve on the oscillogram, it is possible to indicate only the upper limit of the possible values of the decomposition rate. At $T > 5500°$, on the contrary, the decomposition zone is too short, which makes quantitative measurements difficult.

Experiments were carried out with gases subjected to different degrees of purification (removal of condensing impurities was accomplished by cooling in a mixture of dry ice with acetone; purification from noncondensing impurities, by chromatographic separation of gases *). As it turned out, the values of k_{CO_2} obtained in this way do not differ from one another (within the scatter). For technically unpurified carbon dioxide there is a tendency toward somewhat

Fig. 4. Dependence of the logarithm of the constant k_{CO_2} on the reciprocal temperature

Figure 2: Fig. 4. Dependence of the logarithm of the constant k_{CO_2} on the reciprocal temperature

smaller values of k_{CO_2}, but it has not yet been possible to establish a quantitative difference. It is very important to note that the results of measuring the rate of CO_2 decomposition when studying absorption at two different wavelengths ($\lambda_1 = 2380$ Å and $\lambda_2 = 3000$ Å) also coincide, i.e., the result obtained does not depend on the choice of the spectral region. This may indicate that in the present case we are indeed dealing with molecular decomposition.

Fig. 4. Dependence of the logarithm of the constant k_{CO_2} on the reciprocal value of the temperature

Plotting the obtained results in the form of the dependence of $\lg k_{CO_2}$ on $(1/T)$ (see Fig. 4), one can try to estimate the activation energy Q of the reaction under consideration, relying on the Arrhenius formula $k = a\exp(-Q/RT)$. Calculation shows that in our case $Q = 87 \pm 9$ kcal/mole. Interpolation of k_{CO_2} makes it possible in this case, for the mean values of k_{CO_2}, to write approximately the relation

$$k_{CO_2} \approx 1.5 \cdot 10^{14} \exp(-43800/T)$$

$$(\text{cm}^3/\text{mole} \cdot \text{sec}).$$

On the other hand, the activation energy is sometimes assumed to be equal to the bond-dissociation energy (in the present case, the dissociation of the CO_2 molecule into CO and O, equal to $D = 125.7$ kcal/mole), and the pre-exponential factor in the Arrhenius formula is written in the form $a = P(D/RT)^n \cdot \sqrt{T}$. The results obtained in the temperature interval $T = 3000$–5500° K in this case are fairly well interpolated by the relation

$$k_{CO_2} \approx 3 \cdot 10^7 (D/RT)^6 \sqrt{T} \times \exp(-D/RT)$$

$$(\text{cm}^3/\text{mole} \cdot \text{sec}).$$

Moscow State University
named after M. V. Lomonosov

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Note: Figure translations are in progress. See original paper for figures.