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EXPERIMENTAL STUDY OF EFFECTS OF LAMINAR BOUNDARY LAYERS ON CHEMICAL-KINETIC MEASUREMENTS IN A SHOCK TUBE

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ABSTRACT

Rate constants for the reaction

$$H + O_2 \rightarrow OH + O \qquad II$$

were deduced from shock tube measurements obtained in the presence of completely laminar boundary layers. The need for boundary layer corrections and the proper method of applying them were shown by comparing these rate constants with a standard line based on data determined previously in the presence of wholly turbulent boundary layers. The classical shock tube treatment illustrated the need for applying some type of boundary layer correction. The corrections were applied by means of a computer program for a subsonic diffuser, where the area ratio was described by Mirels' equation

$$A_x/A = \left[1 - (x/l_m)^{\frac{1}{2}} \right]^{-1} \qquad (1)$$

The values of l_m used in this equation were calculated by equations supplied by Mirels. These results were very satisfying as they showed excellent agreement with the assumed standard line. A revised value of the rate constant for reaction II is reported. It is $k_2 = 1.38 \times 10^{14} \exp. -16400/RT$.

INTRODUCTION

Mirels (Ref. 1) has suggested that flow non-uniformities induced by the boundary layer behind an incident shock may significantly affect shock tube studies of chemical kinetics. This suggestion has not had a great impact on chemists using shock tubes. The main reason for this is probably the lack of experimental evidence confirming that kinetic data are subject to, and must be corrected for, flow non-uniformities. In a few published instances these corrections were applied. But it was not clear the kinetic data actually required correction, nor that Mirels' treatment was a proper basis for making corrections.

Recently (Ref. 2) we have shown these flow non-uniformities do affect shock tube studies of chemical kinetics when the boundary layer is wholly turbulent. By using the behavior of a well-understood chemical system as a probe, it was established that changing flow conditions behind the shock must be accounted for in order to explain the observations. Mirels' description of the flow was found to be satisfactory for this purpose. With the need for corrections and the method of applying them established, several rates of the chain-branching reactions of the H_2-O_2-CO system were next measured (Ref. 3). The results were very satisfying. This can be judged by the excellent agreement between the line fitted to the corrected data of reference 3, and the results of many other investigations that span a range of 10^{10} in the rate constant of the reaction

$$H + O_2 \rightarrow OH + O \qquad II$$

Figure 1 shows this comparison. These results were obtained in the presence of fully turbulent boundary layers. Whether such agreement can be taken to mean that the results of reference 3 are accurate rather than lucky is unknown. However, for the purpose of this work, it is unimportant; regardless of their absolute accuracy, they may be taken as a standard with which we can inquire how data on this rate, obtained in the presence of fully laminar boundary layers, should be handled.

In short, the purpose of this work is to show whether laminar boundary layer corrrections are necessary and if so, how to apply them.

BACKGROUND

When a mixture of H_2-O_2-CO is suddenly heated, initiation reactions such as

$$H_2 + O_2 \rightarrow 2OH$$

$$CO + O_2 \rightarrow CO_2 + O$$

produce small concentrations of atoms and free radicals. These concentrations then grow exponentially via the branched chain scheme

$$\begin{array}{rcll} OH + H_2 & \rightarrow & H_2O + H & I \\ H + O_2 & \rightarrow & OH + O & II \\ O + H_2 & \rightarrow & OH + H & III \\ H + O_2 + M & \rightarrow & HO_2 + M & IV \\ OH + CO & \rightarrow & CO_2 + H & V \end{array}$$

Theory shows (Refs 4,5) that the oxygen atom concentration increases as $[\,O\,] = A \exp(\lambda t)$ where λ is known as the growth constant. For very rich mixtures such as those used in the present work ($H_2/O_2 = 10$) λ is governed almost entirely by reaction II, i.e. $\lambda \simeq 2k_2\,[\,O_2\,]$

The experimental growth constant was measured by monitoring the carbon monoxide flame band radiation. This was the reason carbon monoxide was added to the H_2-O_2 mixture. When carbon monoxide reacts with atomic oxygen, a characteristic light is emitted. The intensity of this radiation has been found to be proportional to the product of carbon monoxide and atomic oxygen concentrations (Ref. 8). And since very little carbon monoxide is consumed, the light monitors the increase of oxygen atom concentration with time.

Because of boundary layer effects, the distance between the shock and the contact surface tends toward maximum separation and a quasi-steady state of constant velocity (Ref. 1). After this maximum length has been reached, theory shows that the temperature, pressure and residence time of the gas all increase with distance behind the shock. The behavior is identical to that observed in a subsonic flow where the cross-sectional area of the passage is increasing. A computer program (Ref. 9) for a subsonic diffuser was used to simulate the boundary layer effect. In these calculations the area ratio for laminar flow is given by

$$A_x/A = \left[\,1 - (x/l_m)^{\frac{1}{2}}\,\right]^{-1} \qquad (1)$$

where l_m is the length of the hot slug after the shock and contact surface have reached their maximum separation, and x is the distance behind the shock. The relation between gas and laboratory times along with the temperature and pressure profiles were determined from the computer calculation.

EXPERIMENTAL APPARATUS AND PROCEDURE

The tube was a single piece of stainless steel, 5.7 meters long. The internal dimensions were 6.4 x 6.4 cm. with corners rounded to a radius of 1.3 cm. The entire length of the tube was ground to constant inside dimensions and then honed to a highly-polished finish.

Stations for shock-wave detectors were located at 15 cm intervals in the downstream portion of the tube. A thin film gauge, which triggered a raster oscilloscope, was followed by three more thin-film gauges for velocity measurements. Each gauge was connected to an amplifier which differentiated the signal and had a gain of about 2000. These matched amplifiers had a rise time of less than 0.5 microseconds. The output of the amplifiers was processed and displayed on a raster oscilloscope along with microsecond timing markers. In this way, velocities were measured with an uncertainty of less than 0.2%. This was very important since small errors in the shock velocity can cause large errors in the rate constant.

The shock velocity was measured over two intervals and very little attenuation could be observed.

Midway between the last two stations was a pair of 2.5 cm diameter windows made of calcium fluoride and located opposite one another. A thin-film gauge was located to provide an accurate indication of the time at which a shock-wave arrived at the center of the windows and to ascertain that the boundary layer was laminar for the entire test period. All pickups and windows were carefully installed with their surfaces flush with the inner walls of the tube.

The assembled tube could be evacuated to a pressure of about 1 micron and had a leak rate less than 0.2 microns/minute. A liquid nitrogen cold trap in the vacuum line guarded against the possible back-migration of pump oil.

Flame band emission was observed through one of the windows by means of a 1:1 optical transfer system. The filtered (band pass 3700-5600°A) radiation was monitored by a photomultiplier tube. The rise-time of the photomultiplier tube was about 1.5 microseconds. From the opposite window the infrared radiation from hot CO or CO_2 was followed by an infrared monochromotor with an InSb detector. This infrared radiation was used to measure the hot slug length.

The test mixtures (H_2 = .0508, O_2 = .0052, CO = .0508, Ar = .893 and H_2 = .046, O_2 = .0047, CO = .046, CO = .092, Ar = .81) were prepared by the method of partial pressures in stainless steel tanks. Oxygen, argon and hydrogen were research grade gases. Carbon monoxide was condensed at liquid nitrogen temperature; about one quarter of the condensate was discarded with the middle one half used to prepare the sample. Purified dry ice was a convenient source for CO_2.

DATA REDUCTION

Oscilloscope records of light intensity were read on a comparator where intensities (arbitrary units) versus laboratory times were obtained. The relation between gas and laboratory times was determined from the computer calculations. Growth constants λ were obtained from the slope of a semi-logarithmic plot of intensity versus gas time. The temperature and pressure of each experiment was the average over the interval where the slope was measured. These were taken from the computer print out. The measured growth constant, along with temperature, pressure, and other appropriate rate constants, was substituted in the cubic equation (Ref. 3) that relates λ to rate constants and concentrations. The equation was then solved for k_2.

RESULTS AND DISCUSSION

Earlier work showed that rate constants derived from flame band emission were in error if the vibrational relaxation of carbon monoxide was too slow. Because of the low pressures used, there was concern that this might be the case in the present work. Therefore, some data were taken with a mixture containing carbon dioxide so as to accelerate this relaxation (Ref. 3). However, our concern proved to be unfounded and the two test mixtures yielded essentially the same results. Therefore, the reduced data presented in figures 2 and 3 show no distinction between the mixture with carbon dioxide and the one without it.

Figure 2 illustrates the need for some type of boundary layer correction to the data. Here, the laminar data of this experiment and the turbulent data reference 2 have been reduced in the classical shock tube manner. The two sets of data differ markedly. Note that at the temperature where they overlap, the laminar data are about twice as large as the turbulent. This is much larger than any uncertainty in either set of data. This behavior can be rationalized quite nicely by the boundary layer effect. The basic difference in the two experiments is the pressure. In order to obtain runs which had laminar boundary layers, the tube had to be operated at initial pressures about one-tenth those used in the turbulent experiments. Since all the important chemical reactions are bimolecular, their rates depend on the square of the pressure. This means that for the same temperature, the laminar growth constants were measured at a time much greater than the turbulent ones. Therefore, the boundary layer would exert much more influence on these laminar runs than the turbulent ones. Thus when the influence of the boundary layer is neglected, the result is higher rate constants as observed in figure 2.

In the study with a turbulent boundary layer, it was observed that the measured hot slug length was nearly equal to l_m, the maximum separation length. Inasmuch as this behavior was unexpected, it was suggested in reference 2 that measured separations should be used in the reduction of shock-tube data. In accord with this suggestion, the laminar runs were reduced using the measured slug lengths. In this case the area ratio for the subsonic diffuser calculation was determined from equation 1 by setting the value of l_m equal to the measured length. Figure 3a shows the laminar runs reduced in this manner. The circles are the laminar runs while the triangles are the previously determined turbulent ones. The line is the least squares fit to the turbulent data. The laminar data fall well below the line with an activation energy of 18.7 Kcals. Behavior such as this is caused by overcorrecting for the boundary effect. This overcorrecting results from using a value of l_m in the area ratio equation which is too small, thus causing the area ratio to increase too fast and yielding corrections in the temperature, pressure and time stretching which are too large. Consequently, the calculated rate constants are too small and show too large an activation energy.

Since the measured lengths overcorrect the data, the next approach was to reduce the runs with the calculated l_m's. These maximum separation distances between the shock and the contact surface were calculated using Mirels' equation (1). Since 80 to 90%

of the test gas was argon, the value of a numerical factor, β , that is required for the calculation was taken to be that for pure argon (Ref. 1). These calculated l_m's were approximately three times the measured lengths. Rates obtained with the calculated l_m's are shown in figure 3b. Inspection readily shows a much better fit to the standard line. These findings might cause one to question the validity of the turbulent data (Ref. 3) since they were obtained with the measured lengths. However, as we stated in the turbulent study, the measured lengths were within 15% of the calculated ones. And subsequent calculations have shown that a 15% change in l_m yields rates which differ only slightly. In fact, it would be difficult to see a distinction between the points on the graph. Thus, the line fitted to the turbulent data would only show a slight change and certainly would not invalidate any conclusions reached in the present study.

Based on the data presented here, it is concluded that flow corrections for a laminar boundary layer must be applied. The best agreement between the laminar data and the standard line was obtained when the calculated l_m's were used in the data reduction.

Also it should be noted that the scatter in the data is reduced appreciably when boundary layer corrections are applied. This can be seen by comparing figures 2 and 3b.

A least squares fit to all the data in figure 3b yielded $k_2 = 1.38 \times 10^{14}$ exp. $-16400/RT$, which is very similar to the expression for the turbulent data alone, $k_2 = 1.25 \times 10^{14}$ exp. $-16300/RT$. However, because of the wider temperature range covered, this is thought to be a more reliable value of the rate constant.

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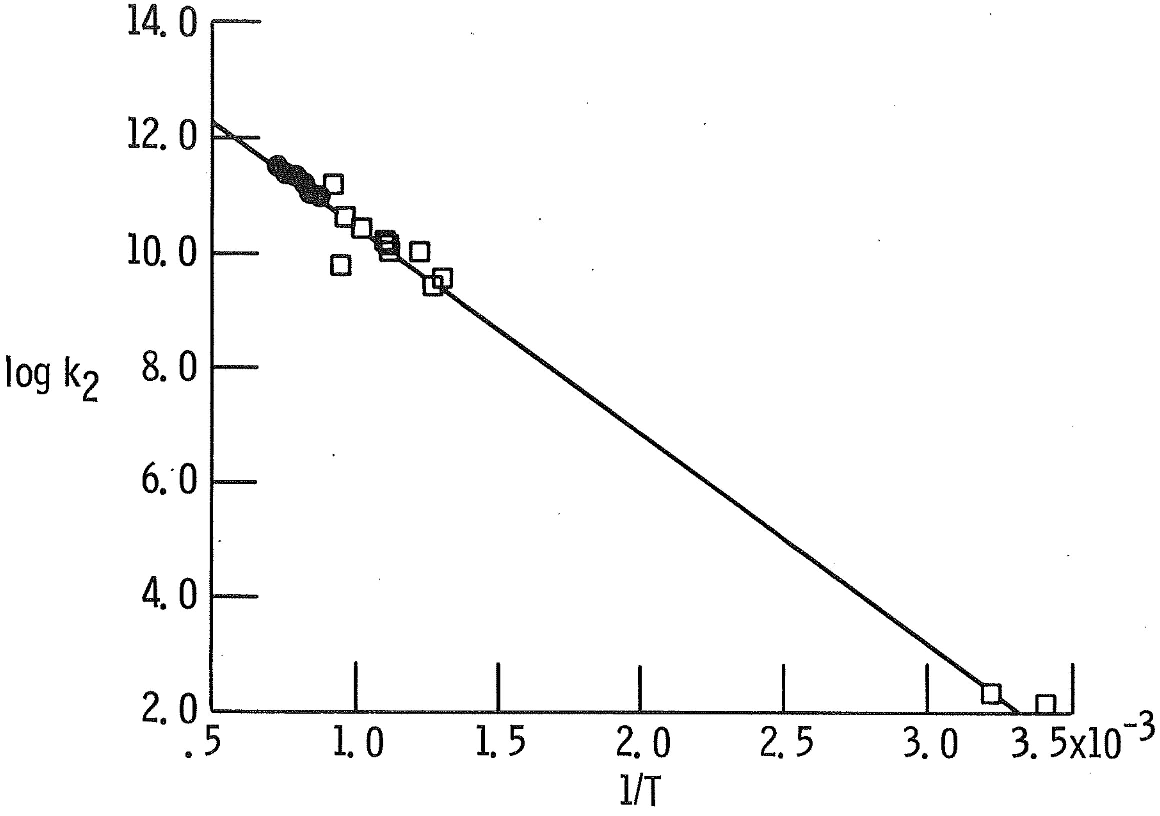


Figure 1. - Arrhenius plot showing comparison between the shock tube data reference 3 (●) and the results of many other investigators (□). The line is the least squares fit to the shock tube data.

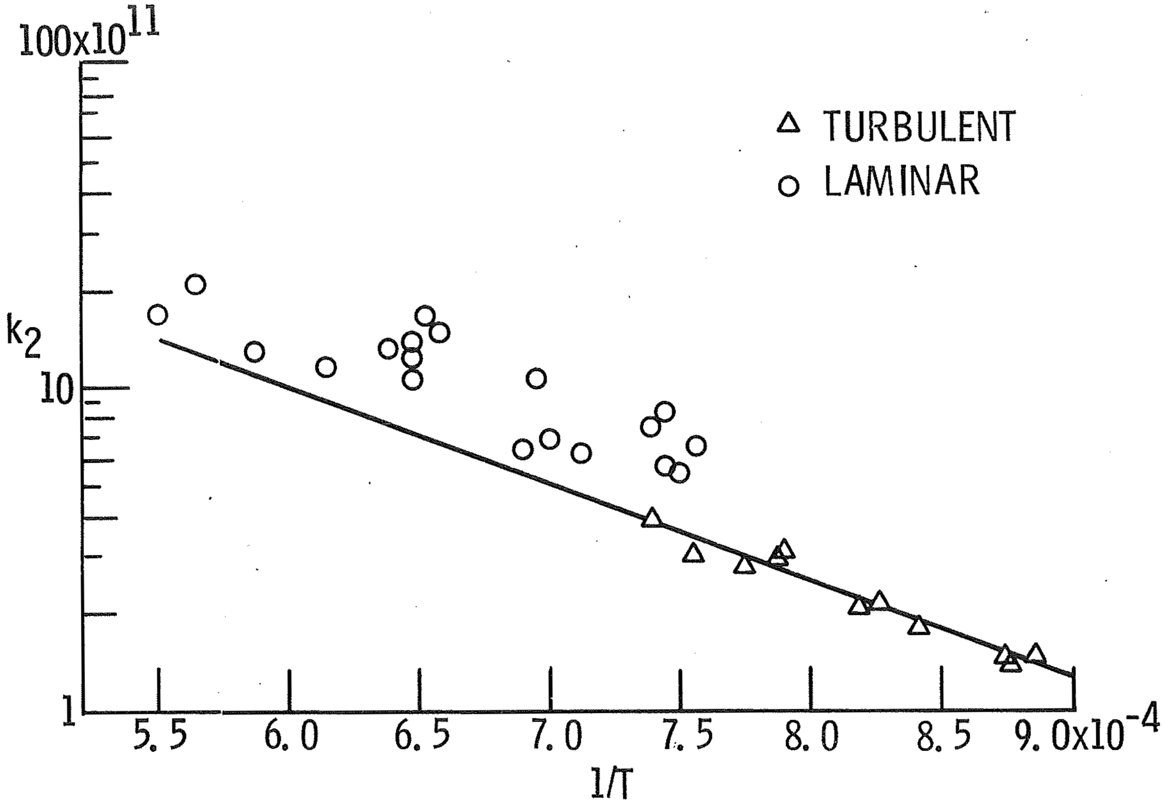
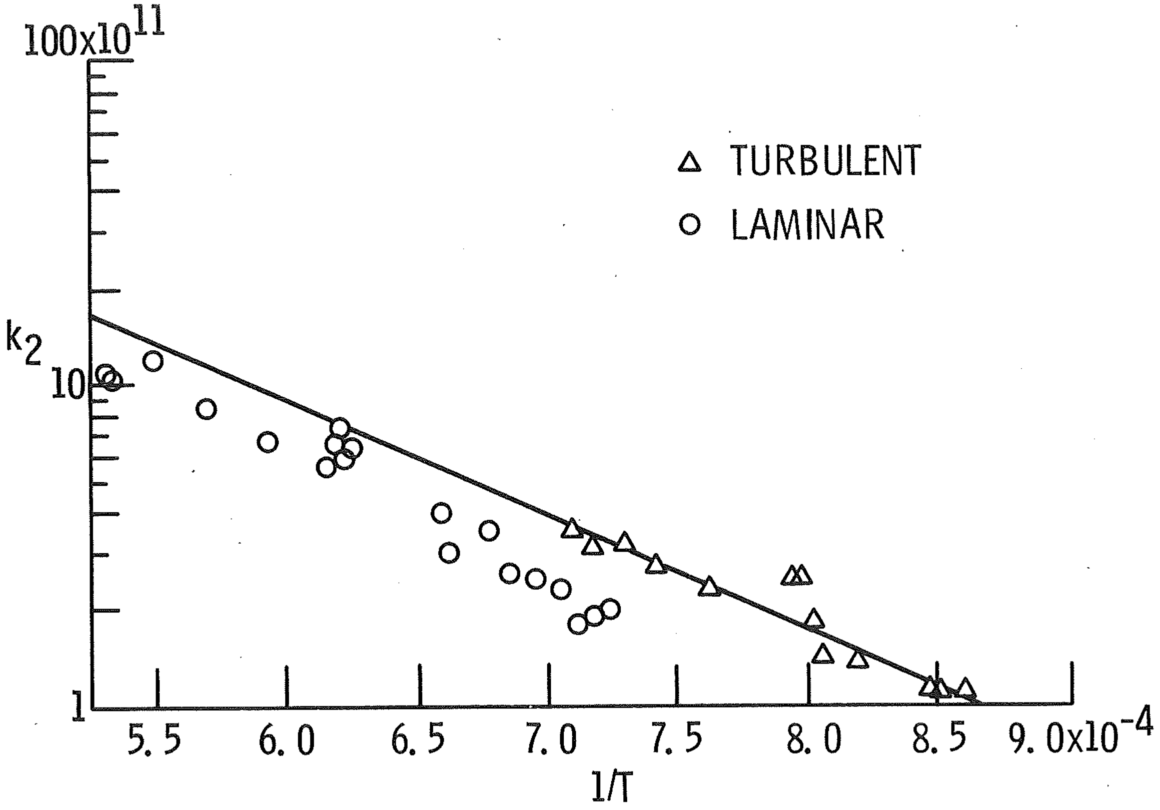
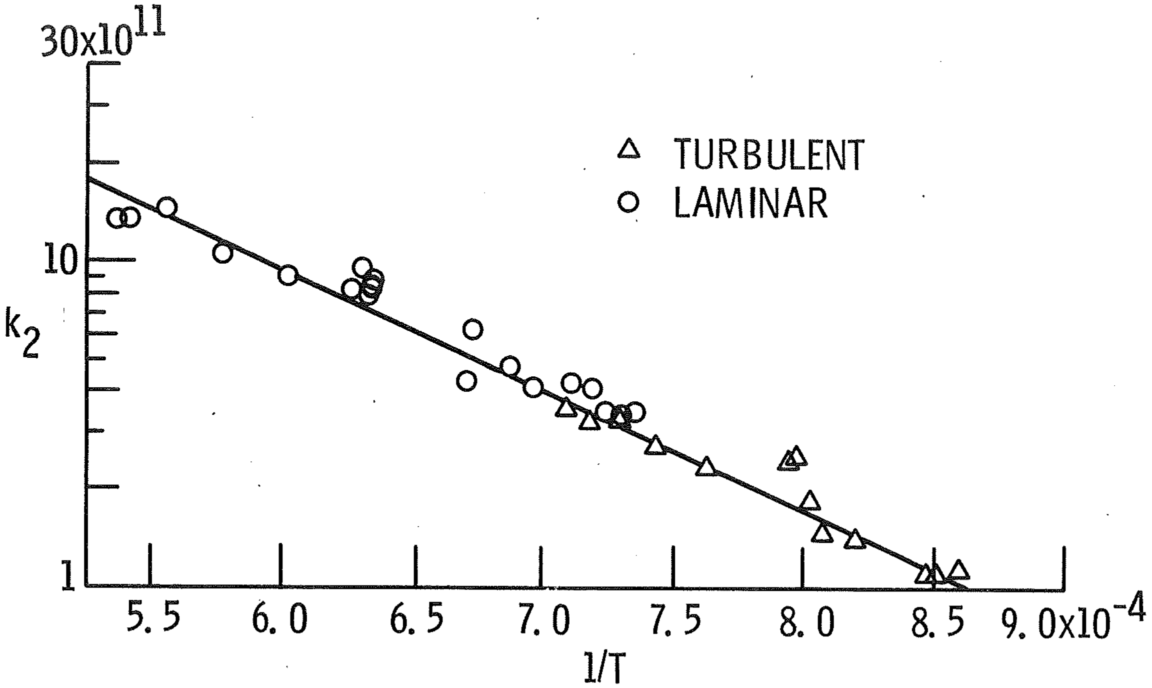


Figure 2. - Arrhenius plot showing comparison between laminar and turbulent data when no boundary layer corrections are used in the data reduction. The line is a least squares fit to the turbulent data.



(a) Measured slug lengths used in the reduction of the laminar data.

Figure 3. - Boundary layer corrected data. The line is a fit to the corrected turbulent data.



(b) Calculated maximum separation length used in the data reduction.

Figure 3. - Concluded.