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Boundary Layer Effects on Chemical Kinetics Studies in a Shock Tube

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The effect of the cold boundary layer on kinetic parameters was studied behind reflected shocks in a single pulse shock tube. By inserting hollow cylinders into the test section, parallel to the tube walls, the surface relative to the volume was increased, and the lowering of the chemical conversion was determined as a function of the surface per unit volume. The test reaction studied was the unimolecular decomposition of perfluorocyclobutane ($C_4F_8 \rightarrow 2C_2F_4$). It was shown that the lowering of the chemical conversion was proportional to the surface-to-volume ratio in the test section. A hypothetical cold layer δ_c in which no conversion occurred was found to be around 0.2 mm. It was concluded that in a shock tube of ~2-in. i.d., at an initial pressure of $p_1 \geq 100$ torr the cold boundary layer has very little effect on kinetic parameters obtained in a single-pulse shock tube. At lower pressures and in smaller diameters shock tubes these effects should be considered when interpreting kinetics results.

I. INTRODUCTION

The shock-tube technique has become very popular in recent years for chemical kinetics studies, but despite the agreement usually found between the data obtained by this technique and by more conventional ones, there are still some doubts as to the accuracy of the method. Ideally, the reflection of a shock from the closed end of a shock tube provides a slug of stationary, high-temperature gas very useful for the study of chemical kinetics. In the real case, however, the presence of the walls of the shock tube causes the buildup of a cold boundary layer (BL) in the hot gas. This cold BL will affect the results of chemical kinetics studies especially if a uniform gas temperature is assumed throughout the gas during the reaction time. In the single-pulse shock-tube technique, where the stationary hot test gas behind the reflected shock is quenched very rapidly, gas samples taken from the shock tube may contain gas from the vicinity of the wall, where the cold BL has affected the reaction rates, as well as from the hotter inner part of the sample. Some investigators have used optical methods to study the presence of the colder, denser gas layer near the walls.[1,2] In the present study, the surface per unit volume of the test section was deliberately increased, and the extent of the chemical conversion was determined for different surface-to-volume ratios. It was possible by this method to elucidate the effect of the boundary layer on chemical kinetics studies and to define the range of validity of the uniform temperature approximation.

As a test reaction we chose the well-studied unimolecular decomposition of perfluorocyclobutane (PFCB) to tetrafluoroethylene (TFE): $C_4F_8 \rightarrow 2C_2F_4$.

II. EXPERIMENTAL

A. The Shock Tube

The 2-in.-i.d. shock tube was operated in a single-pulse mode, described in detail elsewhere.[3] It had a 13-ft Pyrex pipe-driven section divided in the middle by a slide valve. The brass test section located at the end of the driven section was 115.6 mm long and was separated from the glass tubing by a second slide valve. Two high-frequency pressure transducers (Vibrometer type 6-QP-500) connected in parallel, were screwed into the test section flush with the wall and were used for incident shock speed measurements. A signal from a third transducer located just before the second slide valve was used to trigger the upper beam of a Tektronix type 555 dual-beam oscilloscope. The amplified signals (Vibrometer piezoamplifier TA-2/C) from the two pressure transducers were displayed on the upper beam with a time scale of 0.5 msec/cm to show the high-temperature dwell time (~1.5 msec) which was measured to ±5%. The same signals were fed into the lower beam and were displayed at a time scale of 20 μsec/cm. The 5-μsec time marks (generated by a Tektronix type 181 time mark generator) were superimposed on the same beam. A delay for triggering the lower beam was selected to display the signals produced by the incident shock wave passing over the two pressure transducers. The incident shock speed was measured to within ±0.4%. Reflected shock speeds and associated temperatures were calculated from the incident shock speed using the three conservation equations and the ideal gas equation of state. (The latter being justified as the reaction mixture consisted of 99.5% argon.)

B. The Test Section with Increased Surface

In order to increase the surface per unit volume subjected to the hot gas, four hollow cylinders were inserted into the test section, one at a time. The cylinders (stainless steel) were silversoldered to the end plate of the test section. Their lengths were equal to the distance between the end plate and the second slide valve (115.6 mm), leaving a clearance of 0.1 mm when the valve was closed. The cylinders were very thin walled, and their edges were sharpended to minimize the inter-

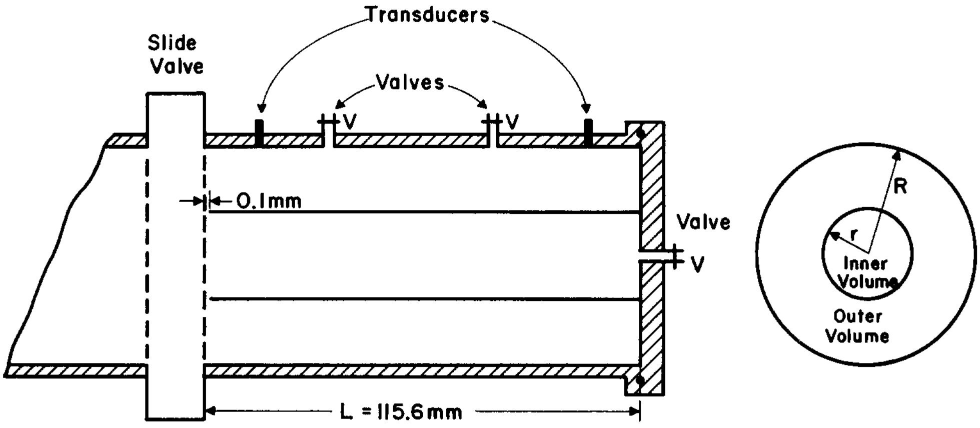

FIG. 1. Drawing of the test section and the experimental setup with the cylinders.

ference with the oncoming shock wave. Two outlet valves were utilized, for gas extraction, one on the test section wall and the other in the center of the end plate. The test section is illustrated in Fig. 1.

The four cylinders used had diameters of 43.1, 38.0, 31.7, and 12.2 mm. Two bulbs for sample extraction were used in each experiment. The ratio of their volumes was equal to the ratio of the volume inside the cylinder (inner volume) to the volume between the outer wall of the cylinder and the shock-tube wall (outer volume), to ensure extraction of the same fraction of gas from the two volumes. The 0.1-mm clearance between the slide valve and the cylinder's end is believed to prevent any mixing of the samples in the two compartments when the two valves were opened simultaneously. It is also assumed that there is a perfect mixing of the test gas in each section after it has been processed, and before it is removed from the shock tube for analysis.

C. Materials and Analysis

The PFCB used in these experiments was obtained from Peninsular Chemical Research Company and was 99.9% pure. It contained no traces of TFE. The argon used was Matheson prepurified grade listed as 99.998% pure. A mixture of 0.5% PFCB in argon was prepared and stored at high pressure (100 psi) in a stainless-steel cylinder. Driver gas was Airco pure-grade helium.

Shocked samples were analyzed for C_4F_8 and C_2F_4 on a Perkin–Elmer 820 gas chromatograph, using a 2-m silica gel column at 150°C, with helium as a carrier gas and a thermal conductivity detector. When the experiments with the cylinders were carried out, two bulbs for sample extraction were used and two analyses for each shock were performed. The analysis of the bulb connected to the center of the end plate gave the chemical conversion in the inner volume whereas the one on the test section wall gave the conversion in the outer volume.

III. THE TEST REACTION: $C_4F_8 \rightarrow 2C_2F_4$

As a test reaction the decomposition of PFCB was studied. The kinetics of its unimolecular decomposition was studied behind reflected shocks in a single-pulse shock tube by two groups of investigators. Lifshitz *et al.*[4] found $k_{\text{uni}}^{\infty} = 10^{16.3} \exp(-74.3\times10^3/RT)$ sec^{-1} for the high-pressure limit rate constant. More recently Simmie *et al.*[5] reported for k_{uni}^{∞} the value $10^{16.0}\times \exp(-75.5\times10^3/RT)$ sec^{-1}, in very good agreement with the previous value. In addition, these two rate constants were in excellent agreement with the ones obtained at lower temperatures in static systems.[6,7] It may therefore be assumed that the rate constant is very well established.

Using the average value of the two rate constants, i.e., $\sim1.5\times10^{16} \exp(-74.9\times10^3/RT)$ sec^{-1}, one can show that if a reaction mixture is heated to 1300°K and maintained at that temperature for a period of 1.5 msec (which is the experimental dwell time in the shock tube), the decomposition will proceed ~99.5% towards equilibrium. Since the reaction is endothermic (ΔH = 49.9 kcal/mol), a mixture of 0.5% PFCB in argon must be heated to ~1350°K in order to end up with 1300°K. The temperature drop (ΔT) during the decomposition is

$$\Delta T = (\%\text{PFCB}\times10^{-2}\times\Delta H)/C_p \approx 50°\text{K}. \quad (\text{I})$$

In addition, the conditions behind the reflected shock are such that *at equilibrium* around 1300°K, 0.5% PFCB in argon, at an initial pressure $p_1 = 100$ torr, will completely decompose (>99.99%) to TFE. Thus, after 1.5-msec dwell time, not more than 0.5% PFCB out of the total fluorocarbon content is expected to remain in a 0.5% mixture initially heated to 1350°K. Any amount of PFCB exceeding 0.5% of the fluorocarbons found in the reaction mixture following the experiment can be attributed to some gas-dynamic disturbance.

IV. RESULTS AND DISCUSSION

A. Experiments without Cylinders

Thirteen shocks were initially run without any cylinder in the test section. The temperature range covered was 1320–1415°K, with initial pressures of 100 torr of the reaction mixture containing 0.5% C_4F_8 in

TABLE I. Summary of the experimental conditions of shocks without cylinders.

Shock No.	T_5(°K)	% Conversion
1	1402	97.0
2	1320	95.5
3	1368	97.0
4	1366	97.0
5	1414	97.0
6	1368	97.0
7	1406	97.5
8	1415	96.6
9	1396	95.6
10	1404	97.0
11	1368	96.3
12	1368	96.3
13	1378	98.0

argon. The shock-heated gas samples were extracted from the test section through a valve (see Fig. 1) and analyzed for C_4F_8 and C_2F_4. The results are given in Table I. The average conversion found in these experiments is 96.7%, i.e., 3.3% C_4F_8 instead of 0.5% is found in the reaction mixture. This additional 2.8% C_4F_8 may result from the effect of a cold boundary layer. However, the possibility that the lowering of the conversion might arise from effects of diaphragm breaking and malformation of the shock wave also exists. It is well known that it takes about 20 tube diameters for the shock to build up. In the first 20 tube diameters therefore, the gas is heated to a much lower temperature than that calculated for the downstream part of the driven section. Consequently, if a collected sample contains gas originating from the first $3\frac{1}{2}$ ft of the tube, its analysis will show a considerable lower conversion due to a mixture of an unreacted gas and a reacted one. This is particularly serious when high extents of reaction are involved. A check for this possibility was performed by utilizing the slide valve in the middle of the driven section. The first half of the driven section, i.e., the section between the diaphragm and the valve was filled with a mixture of argon and CF_4 (very inert molecule) having an acoustic impedance equal to that of the reaction mixture, whereas the reaction mixture (C_4F_8+Ar) was introduced only into the section between the middle valve and the end plate, where a well-established shock wave may be expected. Since the conversion is calculated from the ratio of TFE to PFCB it is immaterial whether the analyzed sample is diluted by argon or by any other foreign material.

In a few experiments run this way, the chemical conversion did not increase; it again ranged between 96% and 97%. Since any cold gas mixed with the reaction mixture after the experiment could not have any effect on the observed chemical conversion, we shall assume that the lowering of the conversion is owing to the effect of the cold boundary layer.

We shall now calculate the chemical conversion near the wall and compare it with the experimental one.

B. Calculation of the Chemical Conversion near the Wall

The BL calculations were done treating the wall as part of an infinite plane and taking into account only the high-temperature dwell time behind the reflected shock, i.e., neglecting the effects of the viscous BL formed behind the incident shock and during the passage of the reflected shock along the test section. This is justified since the latter effects occur in a time short compared with the dwell time behind the reflected shock (about 0.15 msec vs 1.5 msec). The characteristic times of growth of the viscous and the thermal boundary layer are about the same, because the Prandtl number is not far from unity.

The problem of calculating the temperature profile in the thermal boundary layer behind a reflected shock has been treated by Goldsworthy.[8] Following his treatment, we assume that the heat conductivity κ_g of the gas is given with sufficient accuracy by $\kappa_g = k_1 T$ where k_1 is a constant and T the absolute temperature. Furthermore, we assume that temperature changes of the wall material are infinitely small. As shown in Ref. 6, this is equivalent to assuming that $(\rho C_p \kappa)_\infty$ is negligibly small compared with $(\rho C \kappa)_w$, where ρ is the density, C the specific heat, and κ the heat conductivity, while subscript ∞ refers to properties of the gas far from the wall and subscript w to properties of the wall material. The heat equation for the gas is then

$$C_p \rho (\partial T/\partial t) = (\partial/\partial Y)[k_1 T(\partial T/\partial Y)]. \qquad \text{(II)}$$

This equation must be solved under the initial condition $T = T_\infty$ at $t = 0$, and the boundary condition $T(Y=0) = T_w$ at $t > 0$. The solution is[6]

$$\frac{T - T_w}{T_\infty - T_w} = \operatorname{erf} \frac{\psi}{2(k_1 p t / C_p R)^{1/2}}, \qquad \text{(III)}$$

where

$$\psi = \int_0^Y \rho \, dY'. \qquad \text{(IV)}$$

Here, p is the pressure and R is the gas constant. The pressure has been assumed constant throughout the thermal boundary layer. This is a very good approximation for the conditions and times of experimental interest.

In order to carry out the calculations, we need the temperature history $T(t)$ of each gas sample. This function $T(t)$ is obtained by substituting into (III) the appropriate relation $\psi = \psi_S(t)$ for each sample. The relation $\psi_S(t)$ follows by noting that the mass between a given gas sample and the wall remains constant:

$$\int_0^Y \rho \, dY' = \text{constant} = \rho_\infty Y_S(t=0). \qquad \text{(V)}$$

Here, $Y_S(t=0)$ is the original position of the sample. The integral on the left is just $\psi_S(t)$. It follows that the temperature history of each gas sample is given by

$$\frac{T_S(t)-T_w}{T_\infty-T_w}=\operatorname{erf}\frac{\rho_\infty Y_S(t=0)}{2(k_1pt/C_pR)^{1/2}}. \qquad \text{(VI)}$$

Some temperature histories $T_S(t)$ of samples at the initial position $Y_S(t=0)$ and for initial temperature $T_\infty=1350°\text{K}$ calculated using Eq. (VI) are shown in Fig. 2. This T_∞ corresponds to an incident shock of Mach number $M_S=2.24$ in argon at a temperature of 298°K. The pressure p_1 ahead of the incident shock was taken to be 100 torr, as was the case in the experiments performed. The following values have been used[9]:

$$k_1=9\times10^{-8}\text{ cal cm}^{-1}\cdot\text{sec}^{-1}\cdot(°\text{K})^{-2},$$

$$C_p=5\text{ cal mol}^{-1}\cdot(°\text{K})^{-1},$$

$$\rho_\infty=4\times10^{-5}\text{ mol cc}^{-1}.$$

When a chemical reaction occurs in the thermal boundary layer, the basic equation (II) should be modified by adding a term giving the rate at which heat is absorbed or generated by the reaction. The equation can no longer be solved analytically. Although the modified equation may be solved numerically, we found it convenient to use a different method of solution. This method is somewhat simpler to use than a completely numerical method. It uses the temperature profiles obtained with no chemical reaction (Fig. 2) and corrects them by introducing the temperature changes due to the endothermicity of the reaction.

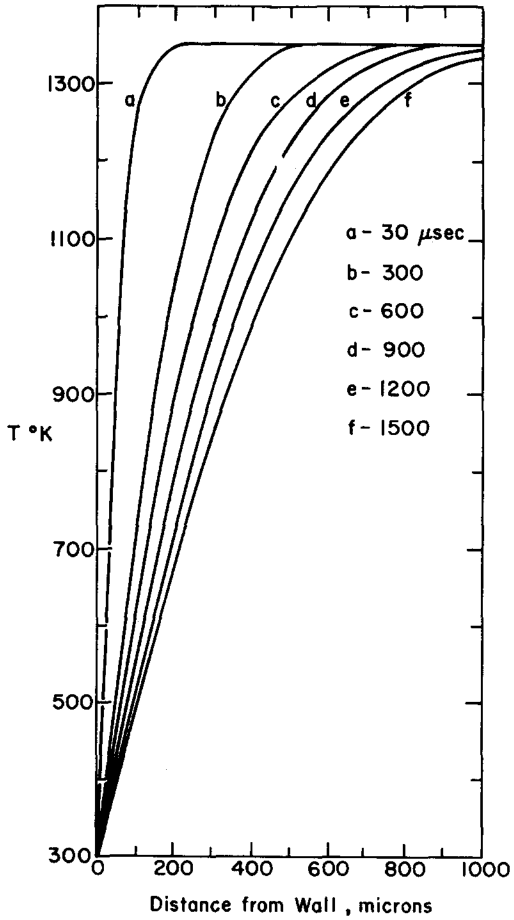

FIG. 2. "Uncorrected" temperature histories $T_s(t)$ of samples at the initial position $y_s(t=0)$ as a function of distance from the wall. $T_\infty=1350°\text{K}$.

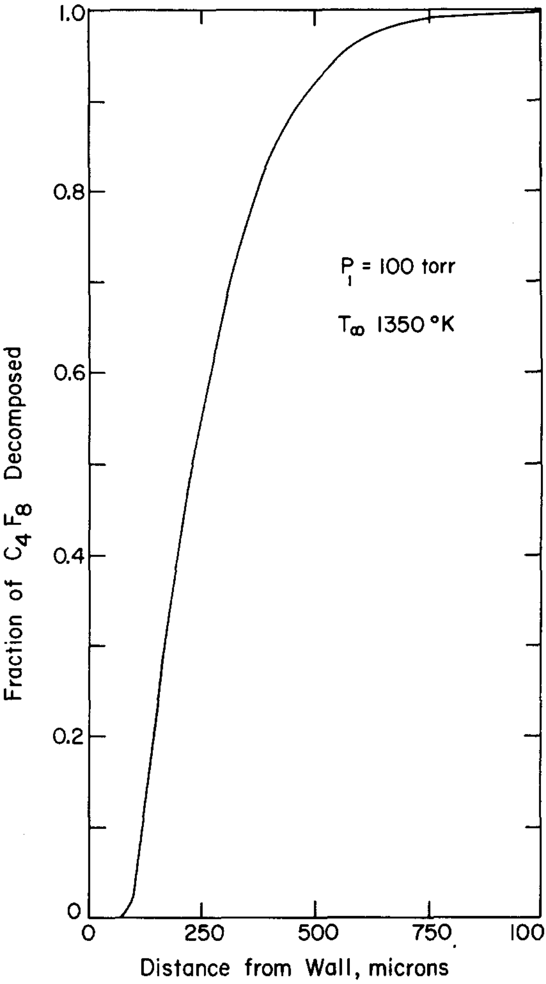

FIG. 3. The chemical conversion at the end of the 1.5-msec dwell time as a function of the distance from the wall.

The chemical conversion which develops during a time interval Δt in each sample is calculated from the equation

$$[1-C(t+\Delta t)]/[1-C(t)]=\exp[-k(T)\Delta t], \qquad \text{(VII)}$$

where $C(t)$ and $C(t+\Delta t)$ are the chemical conversions at the end of a period of time t and $t+\Delta t$, respectively. This equation is the integrated form of the first-order rate equation $dn(t)/dt=-k(T)n(t)$ where $k(T)$ is the first-order rate constant and $n(t)$ is the concentration of the unreacted C_4F_8. The temperature T for the evaluation of $k(T)$ was obtained from the temperature profiles in the following way. If the temperature at a

TABLE II. Summary of the experimental conditions of shocks with cylinders.

Shock no.	Cylinder diam (mm)	T_5(°K)	% Conversion Outer volume	% Conversion Inner volume
14	43.1	1368	83.0	93.0
15		1368	79.5	93.0
16		1386	87.6	94.0
17		1320	87.8	94.7
18		1400	87.6	95.7
19		1398	91.0	95.9
20		1414	91.0	96.0
21		1282	83.5	94.0
22		1386	84.5	95.2
23		1386	88.5	95.6
24	38.0	1414	97.0	97.0
25		1386	95.8	96.5
26		1366	95.0	97.0
27		1386	91.0	95.0
28		1398	90.9	92.8
29		1404	93.5	97.7
30		1386	88.2	94.5
31		1359	88.0	92.7
32		1368	83.7	93.7
33		1328	84.0	89.8
34	31.7	1404	95.7	97.0
35		1358	94.6	94.6
36		1404	96.8	98.1
37		1398	95.6	96.4
38		1386	96.2	97.3
39		1398	96.6	97.4
40	12.2	1416	97.7	92.2
41		1404	97.0	94.5
42		1386	97.0	92.0
43		1349	96.7	88.0
44		1368	97.7	95.3
45		1404	96.0	92.2
46		1378	96.0	92.5
47		1312	90.7	82.4
48		1290	96.5	88.5
49		1368	96.8	95.2
50		1378	96.5	89.7

given distance Y_S at a given time t following the passage of the reflected shock is T, then the temperature used to evaluate $k(T)$ was $T-\Delta T(t)$, where $\Delta T(t)$ is the temperature drop for a conversion $C(t)$,

$$\Delta T(t)=0.5\times10^{-2}\times\Delta H\times C(t)/C_p. \quad \text{(VIII)}$$

To avoid errors in the evaluation of $k(T)$ and hence $C(t)$, which result from the temperature change during the period Δt, the 1.5-msec dwell time was divided into 50 Δt fractions, 30 μsec each, during which the temperature change owing to endothermicity never exceeded several degrees.

By using Eqs. (VI) and (VII), the conversion during each one of the 50 30-μsec fractions was calculated. The value of $C(t+\Delta t)$ for the last fraction gave the conversion at the end of the 1.5-msec dwell time. This procedure was used over the entire test section which was divided for this purpose into annuli each 20 μ thick. Each annulus was considered to have a fixed distance Y from the wall. The "uncorrected" temperature history at each annular slice was similarly obtained by Eq. (VI) (Fig. 2). The resulting conversions at the end of the 1.5-msec dwell time are shown in Fig. 3 as a function of the distance from the wall.

It can readily be seen in Fig. 3 that the conversion is essentially full (i.e., 99.5%) for $Y_S>1$ mm. Thus, the chemical conversion averaged over the entire test section can be evaluated in the following way.

At a distance of 1 mm from the end wall,

$$\langle C_1\rangle=\Delta Y\sum_{n=1}^{50}C_n, \quad \text{(IX)}$$

where C_n is the chemical conversion at a distance of $n\Delta Y$ from the wall and $\Delta Y=0.02$ mm.

In the test section (excluding 1 mm near the end-plate),

$$\langle C_2\rangle=[\pi(R-1)^2\times0.995 + \sum_{n=1}^{50}2\pi(R-n\Delta Y)\Delta YC_n]/\pi R^2, \quad \text{(X)}$$

where R and ΔY are given in millimeters.

The average conversion over the entire test section is then given by

$$\langle C\rangle=[\langle C_1\rangle+(l-1)\langle C_2\rangle]/l. \quad \text{(XI)}$$

The average conversion calculated by Eq. (XI) is 96.5%. This is in very good agreement with the average value of 96.7% found experimentally.

C. Experiments with the Hollow Cylinders

Another way of checking whether the lowering in the conversion is indeed owing to the cooling effect of the cold boundary layer on the shock-tube wall is to increase the wall surface relative to the gas volume.

Thirty-seven additional experiments were run in order to check this possibility. Details of these experiments are given in Table II; the experimental setup is shown in Fig. 1.

Striking evidence that the observed lowering in conversion is indeed related to the BL formed on the

TABLE III. Values of δ_c for the four cylinders used.

Cylinder	Diameter (mm)	$\delta_c(\mu)$
1	43.1	190±70
2	38.0	170±100
3	31.7	160±10
4	12.2	190±100

surface is obtained from Table II. While in the experiments with cylinders 1, 2, and 3 the conversion in the outer volume is always smaller than that in the inner volume, the opposite is true for cylinder 4. The latter is the only instance where the ratio of surface to volume is larger in the inner volume than in the outer one.

An effective thickness of a gas layer in which *no reaction* occurred can be calculated. It should be emphasized that this thickness is by no means the real BL thickness, but only a "chemical displacement thickness" δ_c for these experiments.

The surface per unit volume in the outer space is $F_{\text{out}}=2/(R-r)+1/l$, where R is the radius of the test section (25.4 mm), r is the radius of the cylinder, and l is the length of the test section (115.6 mm). The surface per unit volume in the inner space is $F_{\text{in}}=2/r+1/l$. The difference between the two ratios is $F_{\text{out}}-F_{\text{in}}=2/(R-r)-2/r$. Assuming now an effective thickness distributed homogeneously over the surface, then F, the surface per unit volume, multiplied by δ_c will give the fractional volume occupied by the hypothetical gas layer with no reaction. This gas will contain unreacted C_4F_8; thus

$$F\times\delta_c=0.995-\langle C\rangle. \qquad \text{(XII)}$$

(Note that under the experimental conditions only 99.5% conversion should be observed). Since there are two measurements for each shock, i.e., the conversion in the inner and outer space, δ_c can be computed for each shock from the equation

$$\delta_c=\frac{\langle C_{\text{in}}\rangle-\langle C_{\text{out}}\rangle}{2/(R-r)-2/r}. \qquad \text{(XIII)}$$

Averaging all the shocks, the value of δ_c was found for each cylinder, it is given in Table III.

In shocks without any cylinder the value of δ_c is given by

$$\delta_c=\frac{(99.5-96.7)\times10^{-2}}{(2/R+1/l)}=300\,\mu,$$

which is slightly higher than the values obtained with the cylinders. This slightly high value may result from additional cooling owing to the $C_2F_4\rightleftarrows2CF_2$ dissociation[10] as well as from redimerization of C_2F_4 in the cooling phase. In the cylinder experiments most of the shock parameters and effects just mentioned are canceled by computing δ_c from two measurements made on the same shock, where the only variable is the surface per unit volume. Thus the agreement between the values of δ_c computed with and without cylinders is an indication that the 96.7% conversion measured without cylinders actually arises from the cold BL, which is again in good agreement with the theoretically calculated value of 96.5% conversion.

V. CONCLUSIONS

It has been shown that in the single-pulse shock-tube technique with a shock tube of 2-in. i.d. a conversion of 97% can be obtained at initial pressures of 100 torr. Consequently in any study where only a few percent conversions are reached at the end of the high-temperature dwell time, there is no measurable effect of the boundary layer. The same applies to optical methods for following the course of a reaction, where low extents of reaction are reached and the product concentrations are monitored. A cold BL extending up to 1 mm, even though it is denser than the bulk of the gas, will not affect the emission or absorption appreciably. However, if a high extent of reaction is reached and the remaining reactant concentrations are monitored optically, a considerable effect of the cold BL rich in reactants can be anticipated.

In a small diameter shock tube the relative importance of the BL is increased and should be taken into account. An important parameter also is the pressure level in the shock tube. As seen from Eq. (III), the thermal BL thickness is roughly proportional to the inverse square root of the gas density. Hence at low gas densities the BL is thicker and may cause errors in the data.

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