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EFFECTS OF BOUNDARY LAYER BUILDUP IN SHOCK TUBES UPON CHEMICAL RATE MEASUREMENTS

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ABSTRACT

A theory by Mirels was employed to investigate the effects of boundary layer buildup in shock tubes upon dissociation rate measurements. A comparison was made of bromine dissociation rate constants which had been obtained assuming no boundary layer buildup to those obtained when boundary layer was taken into account. Mirels' wholly turbulent boundary layer case was used in the latter calculations. At low temperatures (1264 K), where reaction rates are low, the measured rate constant increased significantly; while at high temperatures (1827 K), where rates are high, the effect was negligible. In quantitative terms, the activation energy decreased from 31.5 to 30.0 kilocalories (1.32×10^5 to 1.26×10^5 j).

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SUMMARY

The effects of boundary layer buildup in shock tubes upon measured rates of dissociation of bromine were investigated. A comparison was made of rate constants which had been obtained assuming no boundary layer buildup to those obtained when boundary layer buildup was taken into account. The data from a dissociation rate experiment for a 1 percent Br_2-99 percent Ar mixture (ref. 1) were used in this investigation. A theory recently developed by Mirels (ref. 2) was employed to make calculations for the boundary layer case. The wholly turbulent boundary layer form of Mirels' theory was utilized.

Boundary layer buildup affects the variation of flow properties with distance behind the shock as well as particle time-of-flight (reaction time). For chemical rate studies, a knowledge of the local fluid conditions and the true reaction time is essential. However, in the region close to the shock front, where the measurements of reference 1 were made (initial rate measurements used exclusively), the boundary layer corrections on reaction time proved to be negligible.

The influence of Mirels' interpretation of boundary layer buildup upon the measured rate constants was as follows: At low temperatures (1264 K), where reaction rate slopes are shallow, the effect was significant; while at high temperatures (1827 K), where reaction rate slopes are steep, the effect was negligible. The shallow slope changes significantly even for a small displacement of the reaction rate curve, while a similar displacement of a curve which has a steep slope hardly affects the slope. In quantitative terms, the activation energy decreased from 31.5 to 30.0 kilocalories (1.32×10^5 to 1.26×10^5 j).

Although the bromine-argon mixture was the only one intensively investigated, the results are not limited to this particular mixture. Supplemental calculations relating to other noble gas-bromine mixtures indicated that the boundary layer effects would follow the same pattern.

INTRODUCTION

The shock tube has been employed as a useful research tool for many years. In this period, shock tube research has attained a high level of sophistication. Nevertheless, the period of development is not yet over. For instance, in recent years, investigators of shock tubes have become increasingly aware of the departure of this device from ideal behavior.

One area which is receiving increasing attention, and which is the subject of this report, is the effects of boundary layer buildup in shock tubes. In particular, the influences of boundary layer upon chemical reaction rate measurements will be more fully considered than had been possible in the past.

In a recent paper, Mirels (ref. 2) applied a procedure (previously developed by him (refs. 3 and 4)) to calculate the variations of shock tube flow properties between the shock front and contact surface. The calculations were made for the limiting case, where the shock and contact surface have reached their maximum separation. In an ideal shock tube, the distance between the shock and contact surface increases linearly with distance from the diaphragm. However, in an actual shock tube, mass loss to the boundary layer causes the shock and contact surface to approach a limiting distance. In Mirels' treatment of flow nonuniformity in shock tubes, both the laminar and turbulent boundary layer cases are considered.

The growing boundary layer creates, in effect, a diverging duct inside the shock tube through which the shocked gas flows subsonically. This tends to produce increases in pressure, temperature, and density, and a decrease in fluid particle velocity. The decreasing velocity affects the particle time-of-flight, or reaction time; this time is longer than is predicted by ideal shock tube theory. Ideal theory predicts a constant ratio (equal to the density ratio across the shock front, ρ_{21}) between the reaction times and the measured laboratory times. This is strictly correct only at the shock wave.

These boundary layer effects on gas properties and time are particularly important for chemical rate studies where a knowledge of the true reaction time and the local state of the gas is essential. A changing fluid environment affects chemical rates whether brought about by the chemistry itself or by fluid dynamic influences resulting from boundary layer buildup. On the other hand, the boundary layer effect on reaction time is minor as long as rate studies are confined to the initial reaction periods corresponding to the zone close to the shock wave.

The Mirels boundary layer theory treats a well-known shock tube phenomenon which had not been fully appreciated in the past. The present investigation examines the consequences of applying this theory in the translation of kinetic data into rate constants.

Fox, McLaren, and Hobson (ref. 5) made measurements on shocked-gas-flow duration in small diameter shock tubes and concluded that Mirels' theory gives an adequate description of flow duration and attenuation. In addition, their results confirm Mirels' theory of the time dependence of particle paths behind the shock front. The latter conclusion is encouraging because Mirels' basic equation (eq. (1) in the present report, which will be discussed later) is involved in this development. When Mirels proposed this equation (ref. 3), he stated that if the maximum separation distance has not been reached, the equation is less accurate due to entropy variations and the unsteady nature of the flow between the shock and contact surface. However, it now appears that with respect to the particle path accompanying a laminar boundary layer (the conditions of ref. 5) this restriction can be removed. For turbulent boundary layer we must await experimental confirmation.

A final consideration is the applicability of Mirels' boundary layer theory to a dissociating fluid, since the development of the theory assumed no dissociation was occurring in the free stream. For fluids containing a high proportion of dissociating species, this may turn out to be a limitation of the theory. However, in the present case, the small percentage of dissociating bromine should not preclude the use of Mirels' theory.

The present report examines the effects of the predicted flow nonuniformities, due to boundary layer, upon a particular chemical kinetics experiment, the dissociation of bromine in a 1 percent bromine-99 percent argon mixture. In this recent experiment (ref. 1), the rates were obtained from initial slopes of light intensity against time curves (absorption measurements) which were corrected for the influence of endothermicity of the reaction, but not for any boundary layer effects. The chemical kinetic initial profiles have now been corrected for the particular boundary layer effects predicted by Mirels. From these corrections, the effects of boundary layer buildup in the shock tube upon the measured dissociation rate constants were deduced.

DETAILS OF CALCULATIONS

Boundary Layer Buildup

The presence of boundary layer in a moving gas is due to the loss of heat to the walls by conduction, and the loss of momentum due to friction at the walls. From its inception directly behind the shock front all the way up to the contact surface, the boundary layer increases in thickness. Thus the free stream gas behaves as if it were passing through a divergent channel, a subsonic diffuser to be exact. Consequently, the standard nozzle relations could be used provided one had the rate equations for bromine dissociation and recombination and a knowledge of the change in channel cross-section area.

Mirels (ref. 2) developed the following relation to predict the effective area changes for the cases of laminar and turbulent boundary layers for a moving coordinate system in which the shock is stationary.

$$\frac{A_{2s}}{A_2} = 1 - \left(\frac{l}{l_m}\right)^n \tag{1}$$

where $n = 1/2$ for laminar boundary layer and $n = 4/5$ for turbulent boundary layer.

This gives the variation of equivalent free stream cross-sectional area with distance behind the shock. The maximum distance, l_m, is called the maximum separation distance and is achieved when the shock wave and contact surface velocities are equal.

In an earlier paper, Mirels (ref. 4) outlined a method for calculating l_m. This maximum separation distance is a rather complicated function of shock conditions and driven gas physical properties. Because of the complexity of the relations and the uncertainty in physical constants, there is a degree of uncertainty in any calculation of l_m. The calculations of the present report were repeated with l_m's 20 percent higher and 30 percent lower. These calculations not only sought to cover the question of uncertainty in the calculation of l_m for a given system, but were also designed to cover the range of l_m's to be expected if the argon were replaced by other noble gases. Xenon would have a larger separation distance than argon, while neon would have a shorter l_m than argon. The results of these calculations with the higher and lower l_m's indicate that the conclusions of the present paper are insensitive to these variations in l_m.

The turbulent area profile equation was used throughout this study ($n = 4/5$, eq. (1)). The Mirels' theory assumes that either a wholly laminar or a wholly turbulent boundary layer exists in the shock tube. His criteria for applying turbulent theory in the shock tube are conveniently expressed in terms of the product of tube diameter and initial pressure. A turbulent boundary exists when the product of shock tube diameter (in inches) and initial gas pressure (in cm Hg) exceed the following limits: $dp_1 \geq 2$ for $M_s = 3$; $dp_1 \geq 10$ for $M_s = 8$. In the bromine experiments, dp_1 varied from 7 to 30. The range of initial pressures used was 1.8 to 7.2 centimeters of mercury. The shock tube diameter was 4 inches. These conditions coupled with their associated Mach numbers placed the experiments well into Mirels' turbulent boundary layer region. The complete experimental details are described in reference 1.

As a first approximation, the dissociation rate equation previously measured (ref. 1) was the one used to start the calculations.

$$k_D = 2.18\times10^{11}\ T^{1/2} \exp[(-31.5\ \text{kcal/mole})/RT]\text{cc/(mole)(sec)} \tag{2}$$

Detailed balancing was assumed to hold for this system. Consequently, the recombination rate constant was calculated from the experimental dissociation rate constant and the equilibrium constant. The calculations were carried out with a computer program (ref. 6) designed for making nozzle calculations.

For the boundary layer calculations, gas reaction time was related to its corresponding laboratory time by the equation proposed by Mirels (ref. 2). However, corrections on the ideal conversion from laboratory time to gas reaction time proved to be negligible in the region of the initial slope, where all measurements were made.

The familiar Beer's law (eq. (3)) provides the necessary link between the experimental light intensity, I, and the extent of the chemical reaction which is reflected by either $[Br_2]$ or x_{Br_2}, Br_2 concentration or Br_2 mole fraction, respectively.

$$\frac{I}{I_o} = e^{-\epsilon S[Br_2]} = e^{-\epsilon S x_{Br_2}(p/RT)} \tag{3}$$

These relations will be discussed in the Kinetic Analysis section which follows. However, one aspect relating boundary layer buildup and Beer's law should be discussed now.

The cooler boundary layer contributes to the light beam attentuation, as does the free stream gas. This has been known for a long time and was one boundary layer effect with which shock tube research workers did concern themselves. Fortunately for the present experiment, calculations revealed that assuming a constant "S" at conditions of the free stream resulted in no appreciable error. In the region where initial slopes are measured, the boundary layer in thin and the bulk of it is close to the temperature of the free stream. A calculation showed the boundary layer to be approximately 1 percent or less of "S," with 90 percent of it within 5 percent of the free stream temperature. (See Mirels (ref. 7) for the equations needed to calculate the boundary layer temperature profile.)

Kinetic Analysis

Neither bromine concentration $[Br_2]$, nor reaction time, t, the principal kinetic variables, had been measured directly in the bromine shock tube experiments. These were derived from light absorption measurements (4400 Å) of light intensity against laboratory time, I against τ. Beer's law (eq. (3)) relates the experimental variable, I, to the kinetic variable $[Br_2]$. As has been discussed in the INTRODUCTION, the experimental laboratory time, τ, had been converted to the appropriate kinetic time, t, by means of ρ_{21}.

For an ideal gas mixture, equation (3) also indicates the relation between intensity and x_{Br_2}, the mole fraction of bromine. For the present investigation x_{Br_2} is a more useful kinetic variable than $[Br_2]$. Changes in x_{Br_2} reflect only chemical conversion, while changes in $[Br_2]$ occur as a consequence of changes in the fluid properties as well as the result of bromine conversion.

Figure 1 illustrates the effect of boundary layer buildup upon the x_{Br_2} against time curve for a representative run. Both curves shown in this figure were derived from the same experimental intensity against time data. However, for the lower curve, it was assumed that the fluid had passed through a shock tube containing a boundary layer (divergent duct case); while for the upper curve, it was assumed, as in the original bromine experiment, that the boundary layer was absent (constant cross-sectional area case). Both cases start at the same initial conditions of course.

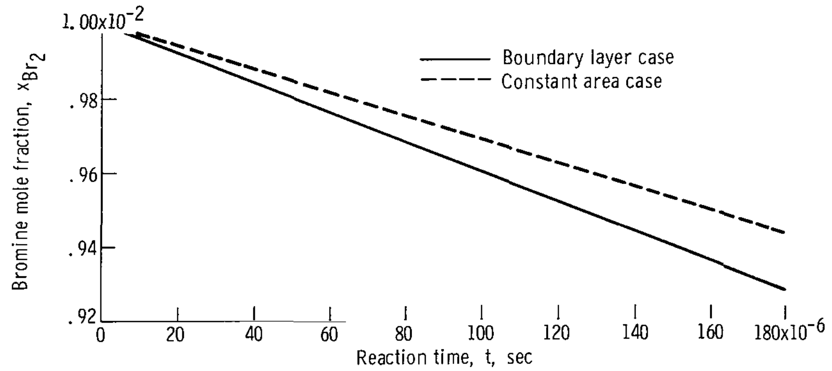
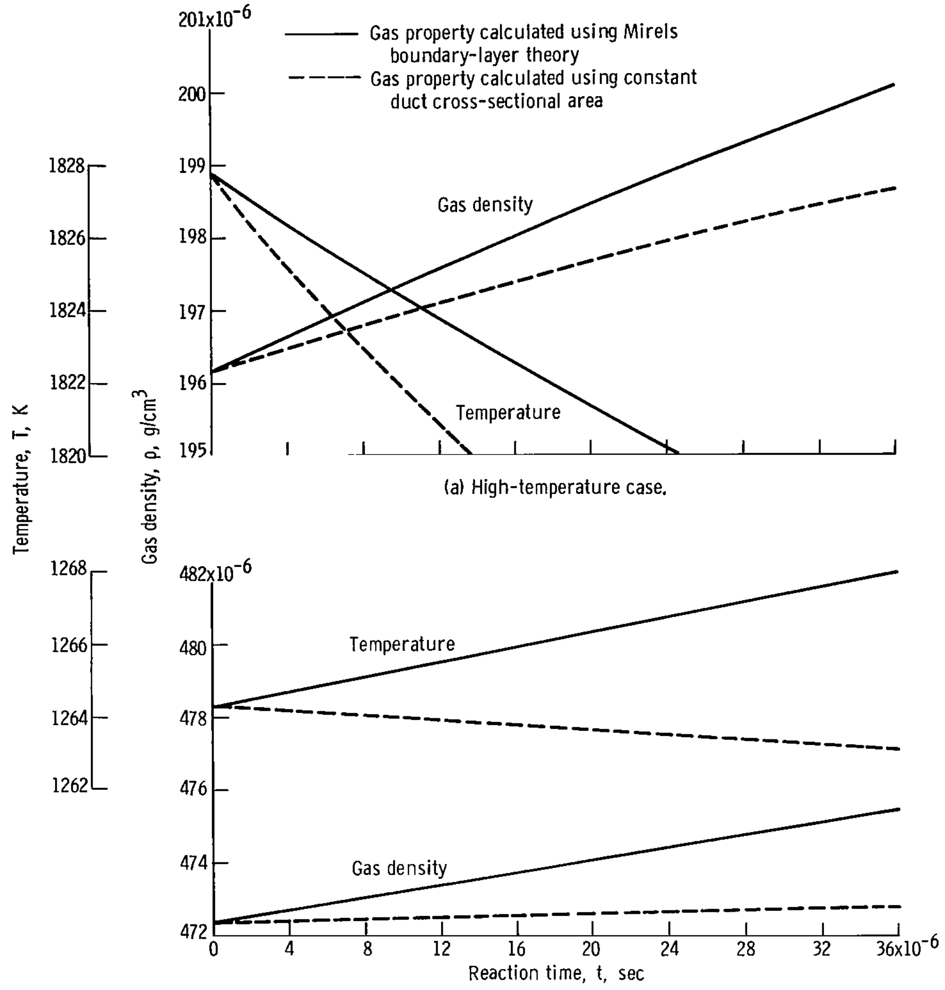


Figure 1. - Comparison of mole fraction - time profiles for boundary-layer and constant-area cases. Curves derived from experimental intensity data.

The conversion of intensity to x_{Br_2} was accomplished by means of equation (3) and two sets of p/RT and ϵ data, one for the constant area case, the other for the boundary layer case. No experimental measurements of the shocked fluid pressure and temperature had been made in the original bromine experiment. Therefore, for each set of initial conditions, the variations of fluid properties with time were calculated. For two runs, corresponding to one high temperature case and to one low temperature case, portions of the boundary layer and the constant area sets of fluid property data are shown in figure 2.

From figure 1 it is concluded, on the basis of the steeper x_{Br_2} against time slope, that the boundary layer case results in a higher rate of dissociation of Br_2. However, the crucial question is, "To what extent is this rate increase attributable to a higher rate constant (k_D) and to what extent is this rate increase attributable to a fluid property vari-



(a) High-temperature case.

(b) Low-temperature case.

Figure 2. - Effect of boundary layer buildup on temperature and density.

able favoring higher dissociation rates?" For instance, in figure 2 we observe that for the boundary layer case, the values of temperature and density are continually higher than the corresponding values of these fluid properties for the constant area case. Both higher temperature and higher densities yield higher dissociation rates. Therefore, from a mere inspection of the relative slopes of the two x_{Br_2} against time curves, one cannot come to any conclusion regarding the differences in the rate constants (k_D) associated with each of the curves, if indeed there are any differences at all.

The manner by which the rate constants associated with the boundary layer cases (at the different initial conditions) were deduced was to postulate values of k_D, calculate an

x_{Br_2} against time curve, and compare it with the corresponding experimentally derived x_{Br_2} against time curve. It was advantageous to use the original k_D for the initial boundary layer calculation. If this calculated curve matched the appropriate experimental curve, it meant that, at these conditions, boundary layer buildup had no effect upon the measured rate constant. If the curves did not match, a k_D which would result in matching could be obtained from the relative positions of the calculated and experimental curves; the initial slopes of these curves are closely related to k_D. The extent to which the new k_D (divergent channel assumption) differed from the original k_D (constant cross-section area assumption) determined the influences of boundary layer buildup upon the measured rate constants.

An alternate procedure was utilized to check the method just described. In two fundamental respects, it differed from the mole fraction method. First, the kinetic variable used was $\ln(I/I_0)$ rather than x_{Br_2}. The choice of $\ln(I/I_0)$ was prompted by the fact that $d\ln(I/I_0)/d\tau$ is directly related to k_D.

$$k_D = \frac{-\left(\dfrac{d\ln(I_2/I_0)}{d\tau}\right)_i \left(\dfrac{V_2}{V_1}\right)_i F}{\epsilon_{2_i} S[Br_2]_i [Ar]_i} \tag{4}$$

The enthalpy correction factor, F, was originally derived by Palmer and Hornig (ref. 8). Hiraoka and Hardwick (ref. 9) have written a convenient expression for this factor:

$$F = \frac{1}{1 - \dfrac{\dot{\rho}_2}{\rho_2}\dfrac{1}{\dot{f}} - \dfrac{d\ln(\epsilon_2 S)}{dT_2}\dfrac{\dot{T}_2}{\dot{f}}} \tag{5}$$

The second difference associated with this alternate procedure was that all the necessary curves were calculated by the computer; none were derived from experiment.

Intensity and x_{Br_2} are of course related, as is evident from equation (2). So despite the differences between the procedures, the results should be the same. Happily, this alternate procedure did check the original one, as will be seen in the next section. The rate constant relation which ultimately brought the mole fraction against time curves together also made the $\ln(I/I_0)$ against time curves coincide.

One of the problems which had to be faced, regardless of the procedure used, was the assurance that the effects determined were due solely to boundary layer buildup and not to other factors such as random error or to incorrect treatment of endothermicity. For instance, the original k_D represents a mean of experimental measurements at various temperatures; in a particular run the measured rate constant may differ from what k_D of equation (2) would predict. In the mole fraction procedure, this was taken into account by adjusting the experimentally derived x_{Br_2} against time slope to account for the error for that particular run. In the alternate procedure, this was not a problem since the machine-computed curves were free of the aforementioned types of errors.

DISCUSSION

The inclusion of Mirels' boundary layer theory in the bromine dissociation data reduction resulted in the following new rate constant:

$$K_D = 1.45 \times 10^{11}\ T^{1/2} \exp[(-30.0 \text{ kcal/mole})/RT] \text{ cc/(mole)(sec)} \tag{6}$$

By comparing this equation with the original rate equation (eq. (2)), one sees that both the activation energy and the preexponential constant have decreased.

The effect of boundary layer buildup upon the apparent rate of dissociation of bromine varied from negligible, at high temperatures (1827 K), to a significant increase at low temperatures (1264 K). This is illustrated graphically in figure 3 in terms of the changes in the initial slope of x_{Br_2} against reaction time. Two sets of lines are shown in this figure. At each temperature, the solid line represents the experimentally derived x_{Br_2} against time variation; the dotted line represents the first boundary layer trial calculation (original k_D used) of x_{Br_2} against time.

The relative positions of the calculated and experimental lines, at each temperature, is a good measure of the effect of boundary layer buildup upon the measured rates of dissociation. In figure 3, for the low temperature case it is apparent that a significantly steeper x_{Br_2} against time line is required for matching; while for the high temperature case the solid and dotted lines are already essentially matched. The steeper slope for the calculated line at the low temperature can only come from an increase in the rate constant, since it develops that, at the 1-percent bromine concentration level, fluid property variation in the experimental case and in all calculated trials are identical. This requires explanation.

It will be remembered that one of the initial steps in this method was to translate the

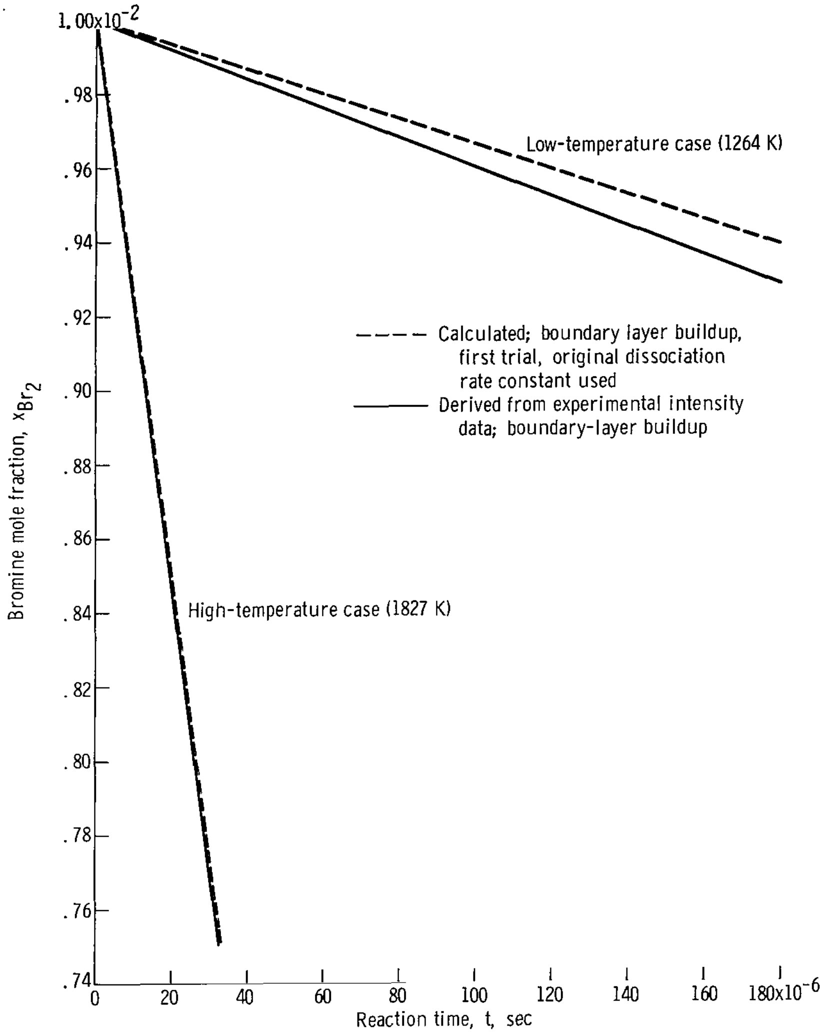


Figure 3. - Initial slopes of bromine mole fraction - reaction time profiles.

experimental intensity against time data into x_{Br_2} against time data. To do this required knowing the variation of fluid properties with time for the boundary layer case. These fluid property data were obtained from the computer calculations of x_{Br_2} against time, examples of which are shown in figure 2. These data were calculated using the original k_D. However, because of the large dilution of bromine by argon in this experiment, the fluid properties such as temperature, pressure, and density are insensitive to the degree of dissociation of bromine. The fluid dynamics due to boundary layer buildup governs fluid property variation; relatively large k_D variation does not change the profiles. In other words, if one were to use the new k_D to generate the fluid property data, for the boundary layer case these would not be significantly different from the solid curves in figure 2. Undoubtedly, for a gas mixture containing a substantial percentage of bromine k_D and the fluid properties would be significantly coupled to require an iterative procedure.

Returning to figure 3 to discuss the results quantitatively, we find that the low temperature slope was affected 18 percent as a consequence of boundary layer buildup while the high temperature slope was only affected 1 percent. These numbers represent the ratio of the slopes of the experimental to the calculated lines at the low and high temperatures, respectively. Apparently the low temperature case is much more sensitive to the effects of boundary layer buildup than is the high temperature case. The shallow slope changes significantly even for a small displacement of the curve, while a similar displacement of a curve which has a steep slope hardly affects the slope.

The high temperature and low temperature runs discussed in this report represent the extremes of the temperature range investigated. Similar treatment of runs at intermediate temperatures produced the expected effect: The boundary layer buildup had an increasingly greater significance for the runs nearer the low temperature end.

The results of the alternate procedure agreed with those of the mole fraction method. In both procedures, k_D expressed by equation (6) brought about matching of the calculated boundary layer line with the appropriate reference line. In the alternate procedure, the $\ln(I/I_0)$ against time line calculated with the original k_D (eq. (2)) for a constant area shock tube represents the reference line. The aim of this procedure was to determine what value of k_D would be associated with the boundary layer case when it traced out the same intensity line as the constant area reference case. This curve-matching procedure required guessing a k_D for the first trail. Figure 4 shows the results of postulating the original k_D for the first boundary layer trial. The same temperatures as before are considered.

The results are comparable with those of the mole fraction method. At the high temperature the lines are matched in the first trial; at the low temperature, the relative positions of the two lines indicates that a larger k_D is required to bring about matching.

In this case, however, the ratio of the slopes is not quantitatively related to the required increase in k_D unless a correction is made for the difference in the boundary layer F factor of the two different low temperature reaction rates. (See eqs. (4) and (5)). Unlike the constant area case, the F factor for the boundary layer case is not a constant calculable from just the initial conditions. It varies as a function of the fluid dynamic effects and the rate of chemical reaction. All of this was immaterial in determining whether or not the alternate procedure checked the major results of the mole fraction method, which of course it did.

Although this bromine-argon mixture was the only one intensively investigated in the present report, the results apply to systems other than this one. Supplemental calculations relating to other noble gas-bromine mixtures indicated that the effects of boundary

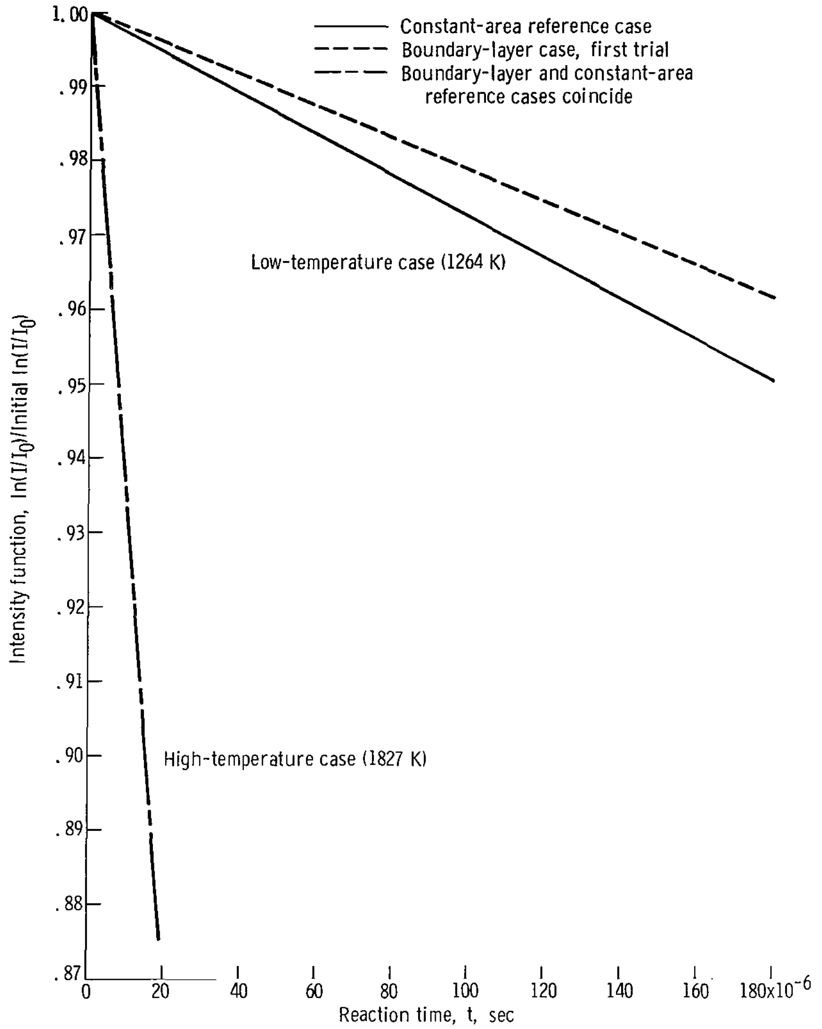


Figure 4. - Calculated intensity function - time profiles. Original dissociation rate constant used.

layer buildup upon bromine dissociation rate measurements made in these mixtures would follow the same pattern.

It is important to remember that this study was made in a dilute mixture of reacting species. One would think that at higher concentrations of reactant, the importance of boundary layer buildup in the same temperature range covered would decrease because of steeper reaction rate slopes.

CONCLUDING REMARKS

The effects of Mirels' theory of boundary layer buildup in the shock tube upon the measured rate constants of dissociation of bromine were as follows: The effect was significant at low temperatures where the reaction rate slope was shallow; it was negligible at high temperatures where the reaction rate slope was steep. The shallow slope changes significantly even for a small displacement of the reaction rate curve, while a similar displacement of a curve which has a steep slope hardly affects the slope.

The direction of the correction was to increase the rate constant. Consequently, the activation energy was decreased from 31.5 to 30.0 kilocalories (1.32×10^5 to 1.26×10^5 j).

Corrections on the ideal conversion from laboratory time to gas reaction time (particle time-of-flight) proved to be negligible in the region of the initial slope, where all measurements were made.

The above remarks are limited to the initial slope technique of rate constant measurements. Certainly if one followed the reaction further toward equilibrium, the effect of boundary layer buildup would have a greater influence.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, May 20, 1968,
129-01-06-04-22.

APPENDIX - SYMBOLS

$[Ar]$	argon concentration
A_2	equivalent cross-sectional area (eq. (1))
A_{2s}	free stream cross-sectional area at shock front
$[Br_2]$	Br_2 concentration
F	Palmer-Hornig enthalpy correction coefficient
$\dot{f}$	time derivative of fraction of dissociation
I	transmitted light intensity
I_o	incident light intensity
I_2	transmitted light intensity through shocked gas
k_D	dissociation rate constant
l	distance between shock front and contact surface
l_m	maximum distance between shock front and contact surface
M_s	shock Mach number
n	exponent in eq. (1)
p	gas pressure
p_1	gas pressure of unshocked gas
R	gas constant
S	optical path length or shock tube diameter
T	absolute gas temperature
T_2	absolute temperature of shocked gas
$\dot{T}_2$	time derivative of absolute temperature of shocked gas
t	reaction or gas time
V_1	velocity of unshocked gas relative to shock front
V_2	velocity of shocked gas relative to shock front
x_{Br_2}	Br_2 mole fraction
ϵ	extinction coefficient of Br_2
ϵ_2	extinction coefficient of Br_2 in shocked gas
τ	laboratory time
$\dot{\rho}_z$	time derivative of density of shocked gas
ρ_{21}	density ratio across shock front
ρ_2	density of shocked gas

Subscript:

i	refers to value of property immediately following passage of the shock

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