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FURTHER STUDIES ON THE DISSOCIATION OF
HBr BEHIND SHOCK WAVES

Norman Cohen, et al

Aerospace Corporation

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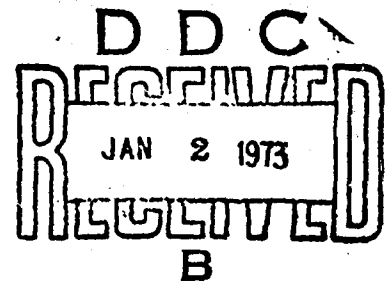
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Further Studies on the Dissociation of HBr Behind Shock Waves

Prepared by
N. COHEN, R. R. GIEDT, and T. A. JACOBS
Aerodynamics and Propulsion Research Laboratory

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Laboratory Operations
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Previously reported shock tube studies of the dissociation of HBr in the temperature range of 2100-4200°K have been extended to lower temperatures (1450-2300°K) in pure HBr. The course of reaction was followed by monitoring the radiative recombination emission in the visible spectrum from Br atoms. The results imply that, in the lower range of temperatures, the activation energy of dissociation can be approximated by the HBr bond energy (88 kcal/mole). It was also found that, in this temperature range, the rate of HBr dissociation is sensitive to the Br₂ dissociation rate and the HBr + Br exchange rate. When these rates were adjusted to bring computed reaction profiles into agreement with experimental ones, it was found that the higher temperature data could also be fitted reasonably well with an HBr dissociation activation energy of 88 kcal/mole, contrary to the conclusions of our previous work, which favored an activation energy of 50 kcal/mole. The "best value" for k_1^{Ar}, the rate coefficient for HBr dissociation in the presence of Ar as chaperone, appears to be $10^{21.78 \pm 0.3} T^{-2.10-88/\theta}$ cc/mole-sec, where $\theta = 2.3 RT/1000$; that for k_1^{HBr} is $10^{22.66} T^{-2.10-88/\theta}$. A detailed review is given of the rate coefficients for the other pertinent reactions in the H₂-Br₂ system, viz., Br₂ dissociation and reactions of HBr with H and Br.		

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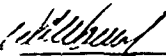
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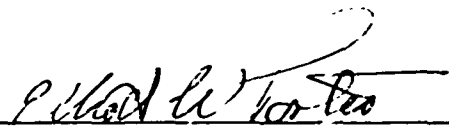
This report, which documents research carried out from July 1969 through June 1972, was submitted 17 October 1972 to Lieutenant Colonel Elliott W. Porter, DYA, for review and approval.

T. A. Jacobs is presently with TRW Systems Group, Redondo Beach, California.

Approved


W. R. Warren, Jr., Director
Aerodynamics and Propulsion
Research Laboratory

Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.


ELLIOTT W. PORTER, LtCol, USAF
Asst Dir, Development Directorate
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I. INTRODUCTION

The chemical kinetics of the hydrogen halogen systems has been the subject of study for about six decades. More specifically, interest in the reactions between hydrogen and bromine dates back to the classic studies in Bodenstein's laboratory in 1906. The early work, however, concentrated on reactions predominant in a starting mixture of hydrogen and bromine; the dissociation of HBr did not receive attention until a decade ago. In this Laboratory, as part of an extended series of investigations of the behavior of hydrogen halides behind shock waves, we previously studied the dissociation of HBr in Ar over the temperature range of 2100-4200°K, using IR emission and UV absorption techniques [1]. It was necessary to invoke a low activation energy (compared with the HBr bond energy) in order best to fit the HBr dissociation data. The activation energy was found to be 50 kcal/mole. HBr was also found to be about 15 times more efficient than Ar as a collision partner in dissociating HBr. In deducing the values for HBr dissociation rate coefficients, it was assumed that the rate coefficients for the other reactions, (2)-(7) of Section IV, were sufficiently well established to be accepted without reexamination. It was believed that a detailed inquiry into the validity of that assumption was unnecessary because, under the experimental conditions of those experiments, the disappearance of HBr was determined almost solely by the direct dissociation reaction.

The purpose of this further study was to determine if the apparent activation energy more closely approaches the bond energy of 88 kcal/mole as the temperature is extended downward. At first, the results of the present experiments were taken to imply that it does. However, as the temperature is lowered, the kinetic analysis of the data becomes more complicated. The high temperature chemistry is sensitive to only the dissociation rate coefficient, but at lower temperatures, the Br_2 dissociation rate and the $\text{HBr} + \text{Br}$ exchange rate play important roles. When these rates were adjusted to bring computed reaction profiles into agreement with experimental ones, it was also possible to fit the higher temperature data reasonably well with an HBr dissociation activation energy of 88 kcal/mole.

II. EXPERIMENTAL

The shock tube and related equipment have been described in earlier work [2]. In all of the experiments reported here, undiluted HBr with a cylinder purity of 99.8% was used. Noncondensable gas contaminants such as air were removed by one distillation step of freezing with liquid N_2 .

In our previous study of HBr dissociation kinetics [1], we followed the HBr concentration change by measuring the IR emission and UV absorption of the HBr molecule. The present experiments were in a temperature range where the equilibrium degree of dissociation is relatively small and HBr concentration is no longer a sensitive indicator of the progress of the reaction. Therefore, a third spectrophotometric technique was used that involved monitoring the radiative recombination emission in the visible from Br atoms. This technique has been reported by several other workers: Palmer [3] with Br_2 , and Araujo [4], Lawrence and Burns [5], and Westberg [6] with HBr. These works demonstrate conclusively that the radiative recombination emission is proportional to the square of the Br atom concentration.

Measurements were made simultaneously at three wavelengths, 5670, 6000, and 6330 Å, from ports located around the perimeter of the shock tube at the same axial position. Three identical optical systems consisted of a sapphire shock tube window, a Suprasil collecting lens, an Optics Technology interference filter (25 Å bandpass), and a RCA Type 6903 photomultiplier. The primary wavelength for data reduction was 6330 Å because of the expected small temperature dependence of emission intensity and the negligible absorption by Br_2 at this wavelength [7].

III. DATA PRESENTATION AND ANALYSIS

The Br radiative recombination emission was recorded at three visible wavelengths during 33 runs when 100% HBr was shock heated to temperatures of 1450-2300 °K and pressures of 1.0-6.3 atm. A typical oscilloscope trace is shown in Figure 1.

The 6330 Å wavelength emission was selected for detailed reaction profile analysis because of the extremely small temperature dependence shown in Figure 2. The slope of the temperature dependence and the experimental scatter are approximately the same as in Westberg's results [6] at 6200 Å. Thus, the measured intensity was set proportional to $[\text{Br}]^2$ without further correction for temperature variations or Br_2 absorption.

By replotting the emission data in a slightly different manner, the slope of the temperature dependence could be used to deduce the electronic states involved [8]. This was not done in Figure 2 because of the extremely small temperature dependence and the possible resultant large error from the scatter shown. Therefore, the assignment of electronic states and choice of banded versus continuum emission are not discussed here. For purposes of this experiment, it is sufficient to establish that the measured emission is proportional to the square of the Br atom concentration.

Seven experimental Br atom profiles chosen from more than 30 runs are shown in Figure 3.

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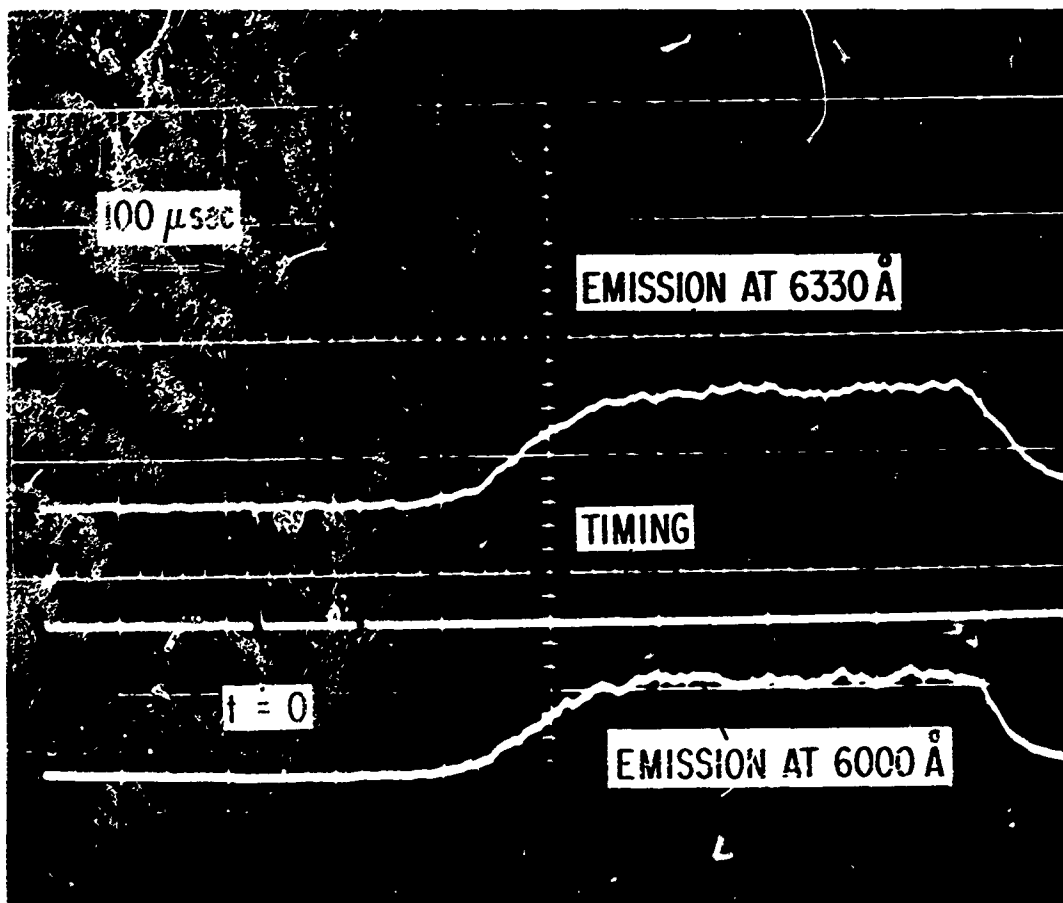


Figure 1. Experimental Records for Run with Initial Temperature and Pressure Behind the Incident Shock 1548°K, 1.87 atm; and Equilibrium Temperature and Pressure 1488°K, 1.89 atm

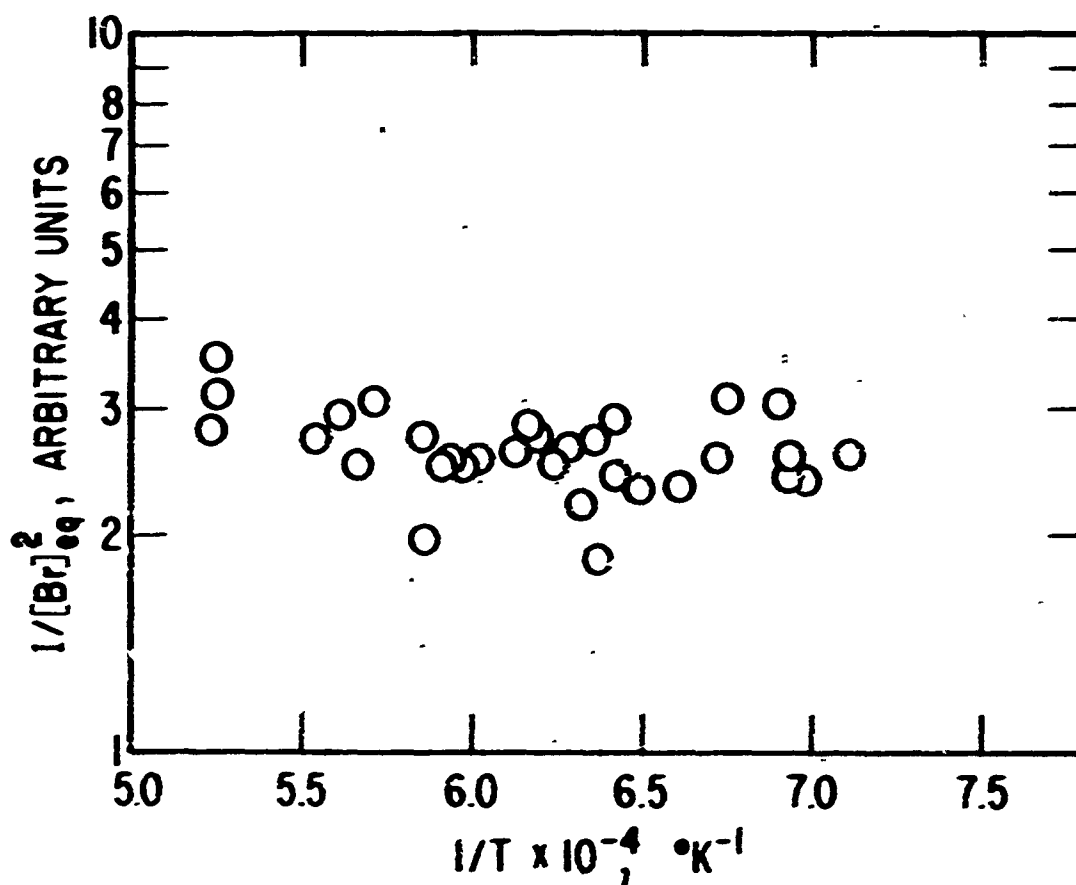


Figure 2. Measured Equilibrium Emission Intensity Divided by the Square of the Equilibrium Bromine Concentration vs Inverse Temperature

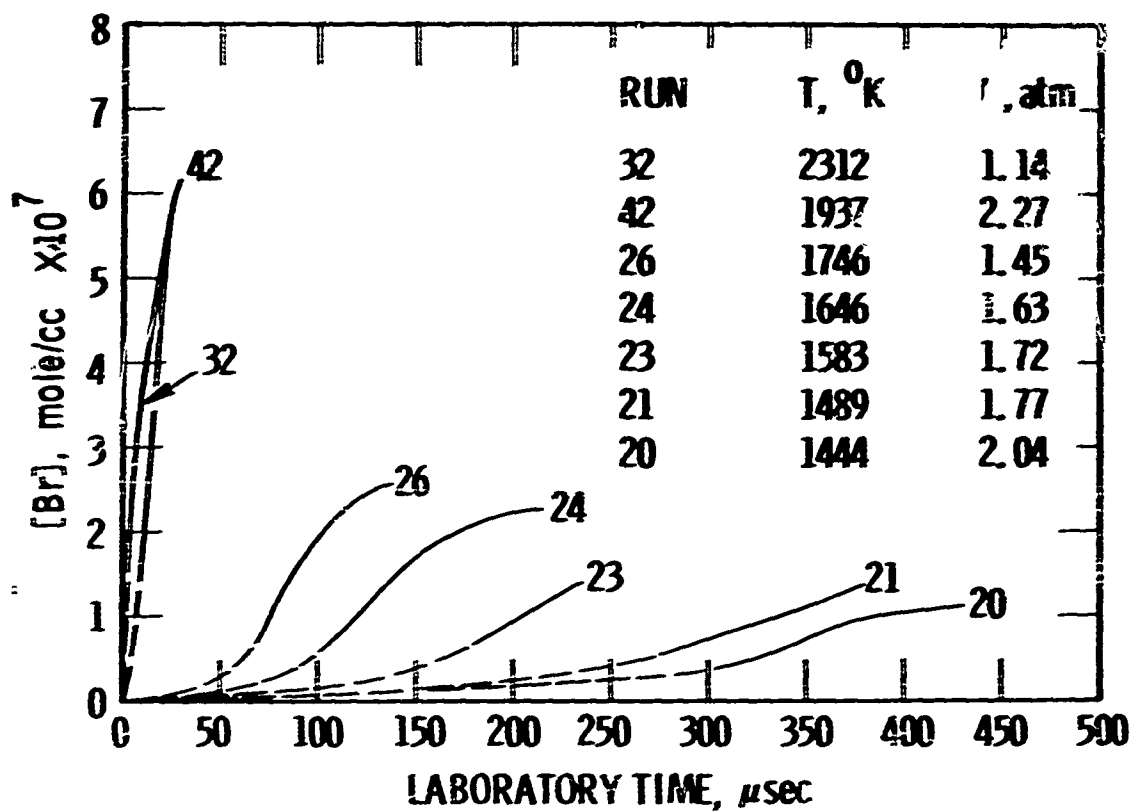
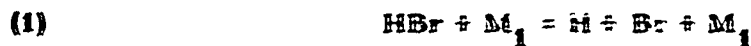


Figure 3. Experimental Bromine Profiles for Seven Runs at Different Initial Temperatures and Pressures

IV. DATA ANALYSIS

For each run, a plot was made of the experimental value of $[Br]$ as a function of laboratory time. Analysis consisted of efforts to match these plots by the appropriate selection of rate coefficients for the following reactions:



M_1 and M_5 are actually of the form $\sum_j a_j X_j$, where the summation is over all species present. $M_3 = Br_2$, $M_4 = Br$, and M_2 is a weighted summation over all other species. The coefficient a_j represents the efficiency of species X_j as chaperone in the indicated reaction. In these experiments, dissociation of HBr was never more than 10%, $[Br_2]$ was always much smaller than $[Br]$, and $[H]$ was always much smaller than $[H_2]$. Thus, it is necessary to sum M_1 and M_5 over HBr and Br only, and M_2 can be taken as just HBr . Hydrogen atom recombination was insignificant under all experimental conditions. Thus, reaction (7) does not need to be discussed further, although it was taken into account in the calculations, and the rate coefficients used were the same as in earlier work [2]. The rate coefficients used for reactions (2)-(7) are discussed in the following section.

V. BRIEF REVIEW OF RATE COEFFICIENTS FOR THE HBr SYSTEM

Although much work has been done on the reactions in the hydrogen-bromine system, and several reviews have been published [9-12], the literature is such a confusing collection of errors, estimates, assumptions, and measurements that we believe another overview is in order. Because of the interrelationships in the experimental determinations, a discussion of the rate coefficients falls naturally into two sections: the exchange reactions, reactions (2) and (3), and the recombination reactions of bromine, reactions (4)-(6). Reaction (7), the recombination of hydrogen atoms, is not discussed further here.

A. EXCHANGE REACTIONS

The first kinetic investigations of the formation of HBr from the elements constituted the classic study of Bodenstein and Lind [13] in 1906. They investigated the thermal reaction over the temperature range of 498-574°K. For 13 years, the complicated kinetics was not explained mechanistically until Christiansen [14], Herzfeld [15], and Polanyi [16] independently proposed the now accepted mechanism that constitutes reactions (2)-(6). The rate law deduced, after some trial and error, by Bodenstein and Lind is

$$\frac{d[\text{HBr}]}{dt} = \frac{k_{\text{exp}} [\text{H}_2] [\text{Br}_2]^{1/2}}{1 + \frac{1}{m} \frac{[\text{HBr}]}{[\text{Br}_2]}}$$

where

$$k_{\text{exp}} = 2 k_{-2} K_{-5,5}^{1/2} \quad , \quad m = k_{-3}/k_2$$

(The notation $K_{a,b}$ signifies k_a/k_b .) They found that reasonable results could be obtained by assuming $m = 10$. Their values, where computed for k_{exp} ,

appeared to be, within experimental error, true rate coefficients and were independent of reactant or product concentrations.¹ Bodenstein and Lind did not extract an analytic expression for k_{exp} from their data nor convert their results to standard units. These tasks were left to later interpreters, of whom there have been many, who have not always agreed with one another.² The expression obtained for k_{exp} by Bodenstein and Lüttemeyer [18] is

$$\log k_{\text{exp}} (\text{cc}^{1/2} \text{mol}^{-1/2} \text{sec}^{-1}) = \frac{8909}{T} + 0.375 \log T + 13.480 \\ - 2.045 \times 10^{-4} T + 2.36 \times 10^{-8} T^2$$

The value of k_{-2} can be extracted from k_{exp} if one knows the equilibrium constant for Br dissociation/recombination, $K_{5,-5}$. This was done by Bodenstein and Lüttemeyer, who obtained

$$\log k_{-2} = 13.862 - 17.64/T,$$

which fitted the experimental data within 9% at all temperatures. By using a revised value for m (based on Bodenstein and Jung [19]) and more modern thermodynamic data, Britton and Cole recomputed k_{-2} from the data of Bodenstein and Lind and obtained

$$\log k_{-2} = 14.357 - 19.37/T.$$

¹ Britton and Cole [17] claim that m actually varies from about 7 to about 12 with the ratio of H_2 to Br_2 , but we have been unable to find evidence for such a statement. In any case, as they note, since a 20% error in m induces only a 3% error in k_{exp} , the values reported by Bodenstein and Lind [13] for the latter rate coefficient are still valid.

² The results of Kassel [9], White [12], and, according to Pease [10], Schumacher (Chemische Gasreaktionen, Dresden, 1938, p. 414), are incorrect.

³ $\theta = 2.3 RT/1000$.

Bodenstein and Jung [19] studied the photochemical formation of HBr at 303 and 575°K and obtained $m = 8.61 \pm 0.3$ at the lower temperature and 8.22 ± 1 at the higher temperature. They concluded that m was temperature-independent, and their mean value of 8.4 ± 0.2 has been used by many later workers as the established ratio of k_{-3}/k_2 . Recently, however, Sullivan [20] reexamined the work of Bodenstein and Jung in light of his own photochemical studies and concluded that they did not measure k_{-3}/k_2 at all, but rather the termolecular reaction



This reaction is negligible in thermal systems in comparison with the accepted chain mechanism.

Bach, Bonhoeffer, and Moelwyn-Hughes [21] studied the reaction of both D_2 and H_2 with bromine, the latter at 549–612°K. After recomputing (not quite correctly) the previous data [13], they found close agreement between the results of Bodenstein and Lind and their own $\text{Br} + \text{H}_2$ results. However, Fettis and Knox [22] have questioned their relative results for H_2 and D_2 on theoretical grounds and on the basis of the analogous H_2/D_2 rates with Cl atoms. The data of Bach, Bonhoeffer, and Moelwyn-Hughes [21], and also of Bodenstein and Lind [13] were recomputed correctly by Pease [10], who used revised thermodynamic data for the Br_2/Br equilibrium. From Pease's recalculations, we can compute

$$\text{Bodenstein and Lind: } k_2 = 10^{14.6} \exp(-20,100/RT)$$

$$\text{Bach et al.: } k_2 = 10^{13.8} \exp(-18,200/RT)$$

Steiner [23] measured the value of k_2 by studying the ortho-para H_2 conversion in the presence of HBr in the temperature range of 821–984°K. In order to extract the desired rate coefficients, the H_2/H equilibrium constant must be known. A modern value for this gives results for k_2 that are about 20% larger than Steiner calculated, and therefore results for k_{-2} that are

about 20% larger than Feltis and Knox gave in their graph of the various experimental results.

A review of the literature of the 1940's and 1950's reveals several other estimates of k_{-3}/k_2 , many of which have later been mistaken for measurements. Cooley and Anderson [24] assumed a value of 8.4 in evaluating their $H_2 - Br_2$ flame studies. Likewise, Levy [25] assumed the same value in his high-temperature (400-1470°K) flow studies. Britton and Davidson [26] reported shock tube studies over the temperature range of 100-1500°K and found the ratio to lie in the range of 5-15.

Britton and Cole [17] examined the reaction between H_2 and Br_2 in a shock tube between 1300 and 1700°K. By monitoring the Br_2 absorption spectrometrically during the course of each run, they were able to calculate the concentrations of products and reactants as functions of time. From these they obtained an experimental rate coefficient $k^{\hat{}} = k_{exp} / [1 + m(HBr)/(Br_2)]$. In separate experiments, shock waves were passed through mixtures of HBr and Br_2 , and the course of reaction monitored as before. If the ratio of k_{-3}/k_2 and the equilibrium constant for Br_2 dissociation are known, the two sets of experiments give direct measures of k_{-2} and k_3 , respectively. Actually, Britton and Cole did not assume the value of k_{-3}/k_2 to be known, but varied it in order to obtain the most consistent set of rate coefficients. At 1300°K, they found the ratio to vary from 9.5 (for mixtures of 1% HBr) to 12.7 (for mixtures of 2% HBr), with an average value of 11.1. At 1700°K, it varied from 8.5 (1% HBr) to 8.2 (2% HBr), with an average of 8.4.

The two most reliable determinations appear to be the recent ones of Fass [27] and Vidal [28]. Fass studied the competition between HBr and Br_2 for H atoms produced by HBr photolysis in the presence of Br_2 at 300-523°K. Combining his results with the high-temperature data of Levy [25], Cooley and Anderson [24], and Britton and Cole [17], he deduced the value of

$$k_{-3}/k_2 = 6.8 \exp(800/RT) \quad .$$

Vidal [28], using essentially the same procedure as Bach, Bonhoeffer, and Moelwyn-Hughes [21], studied the rate of formation of HBr from mixtures of H_2 and Br_2 over the temperature range of 508-566°K. His values for k_2/k_{-3} lay in the range of 10.7-14.4. When his results are added to those of Fass, and the unreliability of the high-temperature determinations is taken into account, a slightly different value for k_2/k_{-3} appears preferable:

$$k_{-3}/k_2 = 5.2 \exp(1100/RT) .$$

These Arrhenius parameters fall nicely between those for Cl and I as tabulated by Fass. This equation for m gives values of 9 and about 6.8 at 1000 and 2000°K, respectively. Using this revised expression for k_{-3}/k_2 and modern thermodynamic data, we can recompute the value of k_{-2} from the data of Bodenstein and Lind and obtain

$$k_{-2} = 10^{13.73} \exp(-17,900/RT) .$$

Except at their highest temperature, the scatter in Bodenstein and Lind's data is on the order of a few percent. If we reject some of the high-temperature results that appear to be spurious, we obtain

$$k_{-2} = 10^{13.97} \exp(-18,500/RT) .$$

The value of k_{-2} was first determined from k_{exp} by Bodenstein and co-workers, as indicated above, and recomputed by Britton and Cole [17] with revised thermodynamic data. Later measurements were made by Bach, Bonhoeffer, and Moelwyn-Hughes [21], Steiner [23], Levy [25], Britton and Cole [17], Britton and Davidson [26], and Vidal [28]. The results were reviewed by Fettes and Knox [22] and more recently by White [12]. On the basis of the data of earlier workers [13, 17, 21, 23, 25], and taking into account the expected difference between k_{-2} and the analogous k for the $D + Br_2$ reaction,

Fettis and Knox concluded that the rate coefficient is

$$k_{-2} = 10^{14.43} \exp(-19,700/RT) \quad .$$

More recently, Vidal has combined his results with those of Bodenstein and Lind [13] and Bach, Bonhoeffer, and Moelwyn-Hughes [21] to obtain

$$k_{-2} = 10^{14.13} \exp(-18,400/RT) \quad .$$

Although the discrepancy between the two equations lies within the experimental scatter when extrapolated to temperatures above about 700°K, the low-temperature discrepancy does not, and Vidal's results are consistently larger than the earlier results [13, 21] by about a factor of 2. The only results above 1000°K are those of Levy [25] and of Britton and Cole [17]. Therefore, the range of uncertainty in their measurements is worth noting. Levy's data, as shown in Figure 5 of Vidal [28] or Figure 1 of Fettis and Knox [22] lead to a range of values for k_{-2} of more than one order of magnitude in the temperature range of 1000-1470°K. The results of Britton and Cole [17] indicate an uncertainty of about 50% in their temperature range.

In our calculations, we use the rate coefficient in the form recommended by Fettis and Knox. However, the preceding discussion should make it clear that, throughout the temperature range of our experiments, there is an uncertainty of 50% in k_{-2} , and hence in k_2 and k_{-3} .

By using thermochemical data from JANAF tables [29], one can fit the equilibrium constants $K_{2,-2}$ and $K_{3,-3}$ within 5% throughout the temperature range of our experiments by the expressions $K_{3,-3} = 2.44T^{0.115} \exp(-42,637/RT)$, and $K_{2,-2} = 0.537T^{-0.055} \exp(16,784/RT)$. The previously discussed values for k_{-2} and k_2/k_{-3} can then be used to obtain expressions for the other atom transfer reactions in the HBr chain. It should be noted, however, that if the value of Fettis and Knox for k_{-2} is combined with $K_{2,-2}$, the resulting value for k_2 is somewhat larger (by a factor of 3.8 at 2000°K and 4.3 at 1500°K) than the value of $1.5 \times 10^{13} \exp(-900/RT)$ reported by Thrush [30].

Thrush also reported a value of $1.5 \times 10^{14} \exp(-900/RT)$ for k_{-3} , which was presumably based on the Bodenstein and Lind value of 10 for m , the ratio of k_{-3}/k_2 . (Both values given by Thrush were referenced to Bodenstein and Muller [31] and to Jost [32]. However, the former authors reported only on the rate of Br_2 dissociation, whereas Jost simply reported the value of $m = 10$ obtained previously and did not evaluate the individual rate coefficients.) In our previous paper [1], we based our choice of k_{-3} on the value given by Thrush. A value larger by approximately a factor of 4 would be more consistent with the value used here for k_{-2} and the assumed value of $k_{-3}/k_2 = 10$. In the calculations described here, most of which were done before Vidal's results were available, we allowed k_{-3} to vary from 1.5 to $6 \times 10^{13} \exp(-900/RT)$ in order to obtain the best fit between computed and experimental curves. In retrospect, it appears that a better choice for k_2 and k_{-3} would have been

$$k_2 = 1.45 \times 10^{14} T^{-0.055} e^{-2,920/RT}$$

$$k_{-3} = 7.5 \times 10^{14} T^{-0.055} e^{-1820/RT}$$

The latter equation for k_{-3} gives numerical values that lie within the range of variation allowed in our computations.

B. DISSOCIATION-RECOMBINATION REACTIONS

The dissociation of bromine molecules has been measured by many investigators under a variety of conditions and in the presence of various different chaperone gases. The results of workers for those M gases pertinent to the experiments described in this work are listed in Tables 1-4. Data for $M = \text{Ar}$ are included, even though our experiments were conducted in pure HBr , because the only estimates for the dissociation rate in the presence of $M = \text{HBr}$ are relative to the rate for $M = \text{Ar}$. Thus, it is important to establish the latter rate as accurately as possible.

The reverse of the dissociation (the recombination of Br atoms) has been studied independently by several workers. It had been generally assumed

Table 1. Bromine Atom Recombination for M = Ar

Source	Temp., °K	k, cc/mole-sec	Technique
J. Katsenovich and M. L. Lohman. ^a	300	2.35×10^{15}	Equilibrium absorption
E. Katsenovich and W. C. Wood ^b			
A. L. Strong and J. E. Willard ^c	300	2.5×10^{15}	Recombination, absorption
D. Brtton and S. Davidson ^d	1600	3.4×10^{14}	Dissociation, absorption
H. B. Palmer and D. F. Hornig ^e	1300	1.0×10^{15}	Dissociation
	2200	1.0×10^{15}	absorption
A. L. Strong, J. C. W. Chen, F. E. Weis, and J. E. Willard ^f	300	3.73×10^{15}	Recombination,
	413	1.4×10^{15}	absorption
A. L. Cavens, Jr., and J. E. Willard ^g	300	2.0×10^{15}	Recombination,
	400	1.1×10^{15}	absorption
D. Brtton ^h	1390	4.4×10^{14}	Dissociation,
	1800	2.3×10^{14}	absorption
G. Burns and D. F. Hornig ⁱ	300	2.3×10^{15}	Recombination,
	450	8.2×10^{14}	absorption
D. Brtton and R. M. Cole ^j	1300	3.4×10^{14}	Recombination
	1700	2.9×10^{14}	and dissociation, absorption
A. Basile and R. L. Strong ^k	300	2.7×10^{15}	Recombination, absorption
C. E. Johnson and D. Brtton ^l	1500	2.2×10^{14}	Dissociation,
	1400	1.5×10^{14}	absorption
M. Marshay ^m	1200	3.4×10^{14}	Dissociation,
	1400	1.5×10^{14}	absorption
T. R. Lawrence and G. Burns ⁿ	1400	2.5×10^{14}	Dissociation,
	2400	0.6×10^{14}	emission
J. K. K. Ip and G. Burns ^o	300	2.6×10^{15}	Recombination,
	1273	2.0×10^{14}	absorption
R. R. Boyd, G. Burns, T. R. Lawrence, and Lippitt ^p	1350	1.4×10^{14}	Dissociation,
	2400	6.0×10^{13}	emission
G. Burns ^q	300	3.0×10^{15}	Recombination, absorption
B. A. deGraff and K. J. Lang ^r	300	2.2×10^{15}	Recombination, absorption

^aTrans. Faraday Soc., 31 689 (1935)

^bTrans. Faraday Soc., 32 907 (1936).

^cAbstracts, Am. Chem. Soc. Meeting, 1954 p. 26R.

^dJ. Chem. Phys., 25 810 (1956).

^eJ. Chem. Phys., 26 98 (1957).

^fJ. Chem. Phys., 26 1287 (1957).

^gJ. Am. Chem. Soc., 81 4773 (1959).

^hJ. Phys. Chem., 64 742 (1960)

ⁱCanad. J. Chem., 38, 1702 (1960).

^jJ. Phys. Chem., 65 1302 (1961).

^kJ. Phys. Chem., 67, 521 (1963)

^lJ. Chem. Phys., 38, 1455 (1963)

^mNAS TN D-3502, 1966, also, J. Chem. Phys., 54 4060 (1971)

ⁿSixth International Shock Tube Symposium, 1967, also, Phys. Fluids, Supplement 1, 109 (1969)

^oDiscussions Faraday Soc., 44 241 (1967) also, J. Chem. Phys., 49 3822 (1968)

^pJ. Chem. Phys., 49 3804 (1968).

^qCanad. J. Chem., 46 3229 (1968)

^rJ. Phys. Chem., 74 4181 (1970)

^snot corrected for effect of 5×10^{-2} Br₂

Table 2. Bromine Atom Recombination for $M = Br_2$

Worker	Temp., °K	k, cc/ mole-sec	Technique
M. Bodenstein and W. Muller ^a	300		Indirect
H. B. Palmer and D. F. Hornig ^b	1600	1.2×10^{15}	Dissociation;
	1000	1.0×10^{13}	absorption
W. G. Givens, Jr., and J. E. Willard ^c	300	260×10^{15}	Recombination;
	400	100×10^{15}	absorption
M. T. Christie, R. S. Roy, and B. A. Thrush ^d	300	48×10^{15}	Indirect;
			absorption
D. Britton ^e	1600	3.0×10^{15}	Dissociation;
			absorption
G. Burns and D. F. Hornig ^f	300	$<50 \times 10^{15}$	Recombination;
			absorption
M. R. Basila and R. L. Strong ^g	300	49×10^{15}	Recombination;
			absorption
G. Burns ^h	300	43×10^{15}	Recombination;
			absorption
R. K. Boyd, J. D. Brown, G. Burns, and J. H. Lippitt ⁱ	1000	6.0×10^{15}	Dissociation;
	3000	$\sim 0.03 \times 10^{15}$	emission
J. K. K. Ip and G. Burns ^j	825	4.2×10^{15}	Recombination;
			absorption
B. A. deGraff and K. J. Lang ^k	300	44×10^{15}	Recombination;
			absorption

^aZ. Elektrochem., 30, 416 (1924).^bJ. Chem. Phys., 26, 98 (1957).^cJ. Am. Chem. Soc., 81, 4773 (1959).^dTrans. Faraday Soc., 55, 1139 (1959).^eJ. Phys. Chem., 64, 742 (1960).^fCanad. J. Chem., 38, 1702 (1960).^gJ. Phys. Chem., 67, 521 (1963).^hCanad. J. Chem., 46, 3229 (1968).ⁱJ. Chem. Phys., 49, 3822 (1968).^jJ. Chem. Phys., 51, 3414 (1969).^kJ. Phys. Chem., 74, 4181 (1970).

Table 3. Bromine Atom Recombination for M = Br

Worker	Temp., °K	k, cc/ mole-sec	Technique
D. Britton ^a	1400	4.4×10^{15}	Dissociation; absorption
R. K. Boyd, G. Burns, T. R. Lawrence, and J. H. Lippiatt ^b	1600	3.5×10^{15}	Dissociation; emission
R. K. Boyd, J. D. Brown, G. Burns, and J. H. Lippiatt ^c	2240	0.35×10^{15}	Dissociation; emission
	1000	200×10^{15}	Dissociation; emission
J. K. K. Ip and G. Burns ^d	3000	$\sim 0.03 \times 10^{15}$	Recombination; absorption
	1200	$4-14 \times 10^{15}$	

^aJ. Phys. Chem., 64, 742 (1960).^bJ. Chem. Phys., 49, 3804 (1968).^cJ. Chem. Phys., 49, 3822 (1968).^dJ. Chem. Phys., 51, 3414 (1969).

Table 4. Bromine Atom Recombination for Various M

M	Worker	Temp., °K	k, cc/mole-sec
H ₂	E. Rabinowitch and H. L. Lehman; ^a E. Rabinowitch and W. C. Wood ^b	300	3.95 × 10 ¹⁵
HBr	M. Bodenstein and G. Jung ^c	300	7.2 × 10 ¹⁵
HBr	D. Britton and R. M. Cole ^d	1300-1700	k _{HBr} ≈ 1.1 - 1.3 k _{Ar}
HBr	K. Westberg and R. F. Greene ^e	1500-2700	k _{HBr} ≈ 3 k _{Ar}

^aTrans. Faraday Soc., 31, 689 (1935).

^bTrans. Faraday Soc., 32, 907 (1936).

^cZ. Physik. Chem., 121, 127 (1926), as recalculated by J. H. Sullivan, J. Chem. Phys., 49, 1155 (1968).

^dJ. Phys. Chem., 65, 1302 (1961).

^eThe Aerospace Corp., El Segundo, Calif., TR-0172(2240-20)-1 (1972), also J. Chem. Phys., 56, 2713 (1972).

that the separately measured dissociation and recombination rate coefficients were related, under all experimentally attainable conditions, by the thermodynamic equilibrium constant. Recently, Burns and co-workers [33-36] have compared dissociation measurements made by following the disappearance of Br_2 through absorption spectroscopy with those made by monitoring Br atom formation as determined by two-body Br recombination emission. By comparing the temperature regime where the two types of measurements overlapped (1300-2000°K), they found agreement above 1600°K but noted that, below 1500°K, the rate coefficients obtained from the absorption measurements were consistently larger (as much as a factor of two) than those obtained from emission studies, with the discrepancy increasing as T decreased (Fig. 4). In addition, they found that the emission measurements implied recombination rate coefficients that were related to the dissociation rate coefficients by the equilibrium constant, whereas the absorption measurements did not. They proposed a theory to account for these interesting observations. We should note that, according to our conversion of Warshay's data [37] from dissociation to recombination rate coefficients, at the highest temperatures his results yield smaller rate coefficients than those of Burns and co-workers as shown in Figure 4. The discrepancy appears to be significant, contrary to the report of Boyd et al. [34] that, at high temperatures, the absorption and emission techniques yield identical results. However, this only strengthens the conclusion that the temperature dependences of the two techniques are significantly different.

Although we are not confident at this time that the theoretical implications of the foregoing facts are resolved beyond dispute, we would expect the results obtained by the emission technique to be more appropriate to our work inasmuch as we also followed the course of the reaction by bromine atom-atom emission.

In the temperature regime of interest here (1400-2200°K), the shock-tube emission data of Boyd et al. [34] (see their Figure 4) can be fitted within about 20% by the expression $\log k_{-4} = 20 - 1.8 \log T$. In our earlier paper [2], the value of k_4 reported by Warshay was chosen for the computer calculations,

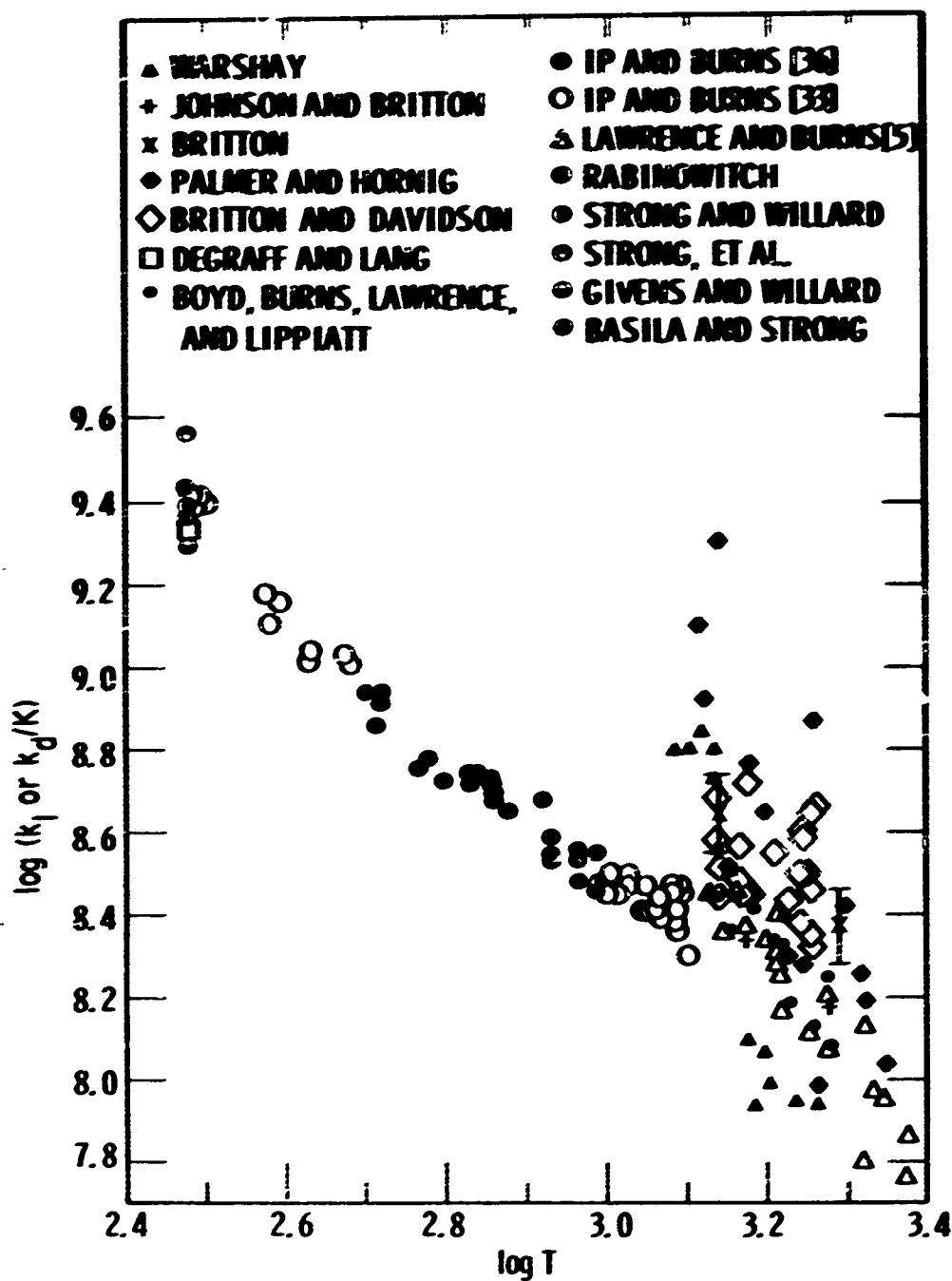


Figure 4. Experimental Rate Coefficients for Bromine Atom Recombination in the Presence of Argon as Obtained by Various Workers

viz., $k_4 = 2.18 \times 10^{11} T^{1/2} \exp(-31,500/RT)$. This led to values of k_4 slightly larger (by a factor of 1.6 at 1400°K) than those given by the above equation below 1600°K and slightly smaller above 1600°K. However, in attempting to match the experimental profiles, we found that the expression of Boyd et al. gave values of k_4 that were too small at the low end of our temperature range. Therefore, we returned to the expression of Warschay.

Because in this work we are interested in k_4 with $M = \text{HBr}$ rather than Ar , it is necessary to know the relative efficiencies of HBr and Ar . As indicated in Tables 1-4, there is not very much information on HBr efficiency. At room temperature, the data of Bodenstein and Jung, as reinterpreted and recalculated by Sullivan, indicate that $k_4^{\text{HBr}}/k_4^{\text{Ar}} \approx 2.6$. The high-temperature results are quite imprecise. Britton and Cole found an approximate value for the ratio of 1.1-1.3. Westberg and Greene [36], in order to match their experiments with computer-generated profiles, required a ratio of approximately 3, where k_4^{Ar} was the result of the work of Warschay [36]. We began our computer calculations assuming that $k_4^{\text{HBr}}/k_4^{\text{Ar}} = 1$ and then varied that value to obtain the optimum fits.

Although k_5 and k_6 , the dissociation rate coefficients for Br_2 in the presence of Br_2 and Br , respectively, are subject to some uncertainty, an examination of the experimental conditions of the various runs indicated that neither of these two reactions was significant in any case. For example, at the low end (1400°K) of the temperature regime, the extent of HBr dissociation never exceeded 1%. Therefore, a value of $k_6/k_4^{\text{HBr}} = 100$ would be required in order for reaction (6) to contribute to the chemistry. Boyd et al. [35] reported a value of $k_6 = 8.8 \times 10^{38} T^{-7.3}$, which implies a value of $k_6/k_4^{\text{Ar}} = 30$ at 1400°K (assuming the emission-measured value for k_4^{Ar}). However, Ip and Burns [36] later preferred $k_6 = 7.1 \times 10^{28} T^{-4.3}$, which is smaller by about a factor of 3 at 1400°K. Since $k_4^{\text{HBr}}/k_4^{\text{Ar}}$ is certainly greater than unity (and probably close to 3), it is apparent that reaction (6) will contribute less than 30% (and probably less than 10%) to bromine dissociation, a fraction that is easily lost in the uncertainty of k_4 . At the high end of the temperature range, i. e., 2300°K, decreasing to 1900°K by the end of the run, the fraction of HBr

dissociated approached 10%. At this temperature, Boyd et al. reported $k_6/k_4^{Ar} = 5$; Ip and Burns reported about the same value. For such runs, our analyses never extended as far as equilibrium. Thus, again the contribution of reaction (6) was less than the uncertainty in the rate of reaction (4).

In all our experiments the concentration of Br_2 was less than 30% of that of Br atoms. Since k_5/k_6 was surely less than 1, the contribution of reaction (5) could be ignored in all cases.

The possible contributions of $M = H$ and $M = H_2$ to Br_2 dissociation remain to be considered. The concentration of H_2 is generally somewhat smaller than that of Br. The only available experimental data on k_7 are at room temperature and imply that $k_7^{H_2}/k_7^{HBr} = 0.6$. Therefore, we can expect no important effect in our calculations from H_2 although we do include the reaction and assume that the above ratio is unity in our temperature range. The concentration of H atoms is always less than that of Br atoms by a factor of 30 to 10^4 . Therefore, we neglect any possible contribution. Thus, we are that the only chaperone species that contributes measurably to Br_2 dissociation in our experiments is HBr.

VI. RESULTS AND CONCLUSIONS

In our earlier work on HBr dissociation, over the temperature range of 2100–4200°K, it was found that the data were fitted much better by an activation energy for HBr scission of 50 kcal/mole than by one of 88 kcal/mole, the HBr bond strength. However, when rates B or C of [1] were applied to the data from the present study, conducted over a temperature range of 1450–2300°K, it was found that the experimental appearance of Br atoms was much slower than the calculations indicated. This implied that the 50 kcal/mole value was not appropriate in this low temperature range (Figs. 5 and 6). On the other hand, rate A, which differed from the "best set" rate C in that k_1 had an 88 kcal/mole activation energy and a lower efficiency for $M = \text{HBr}$, could not fit the data either. Adjustment of the preexponential term of k_1 did not help sufficiently. In order to fit the Br atom profiles, it was necessary to alter one of three rate coefficients, or some combination of the three: either k_1 , k_3 , or k_4 had to be increased at the low end of the temperature range (1450–1500°K). This implied that the activation energy for HBr dissociation was slightly less than 88 kcal/mole, possibly near 80 kcal/mole, or that the values assumed for k_3 and k_4 in our earlier work [1] were incorrect. The results of a lengthy series of curve matching and parameter variations led to the conclusions that the experimental data down to about 1550°K could be fitted fairly well by rate constant N listed in Table 5. The significant differences between rate N and the previous best rate C are: (1) the activation energy k_1 is raised to 88 kcal/mole, and the ratio of efficiencies, $k_1^{\text{HBr}}/k_1^{\text{Ar}}$, reduced from 15 to 3.75. (2) k_3 is four times the previous value, which is the upper end of the variation considered in Section V, and (3) k_5 is unchanged, which means that if the emission data of Boyd et al. for estimating k_4^{Ar} were correct, then $k_4^{\text{HBr}}/k_4^{\text{Ar}} = 1.5$. Figures 7 and 8 illustrate the comparison between experimental profiles and several computed profiles for two representative runs. In order to fit the data between 1550 and 1450°K, it was necessary either to increase k_4 by a factor of 2 (rate P, Table 5) or more, or to increase

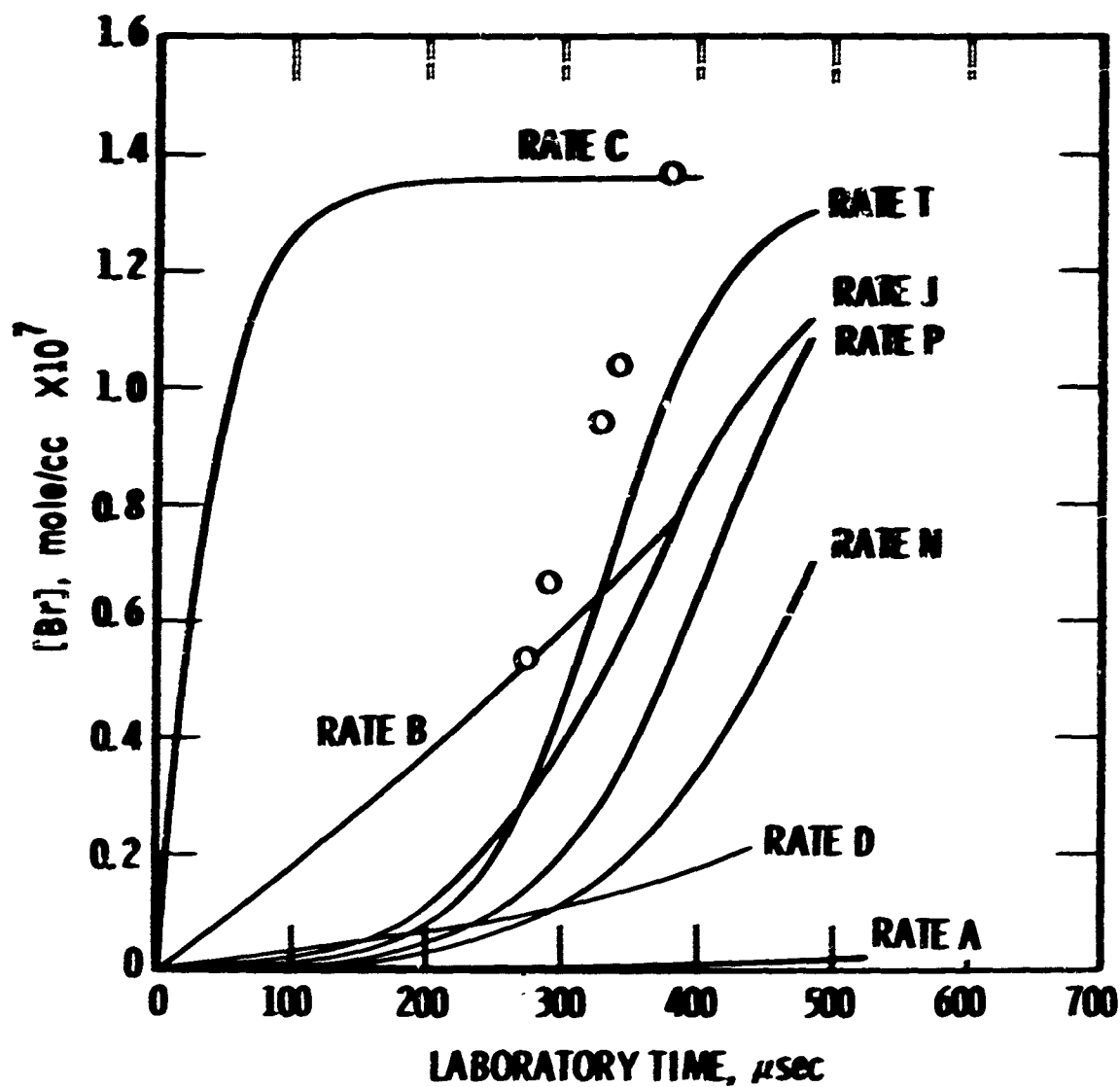


Figure 5. Comparison of Experimental Bromine Profile for Run 21 With Computed Profiles for Various Sets of Rate Coefficients

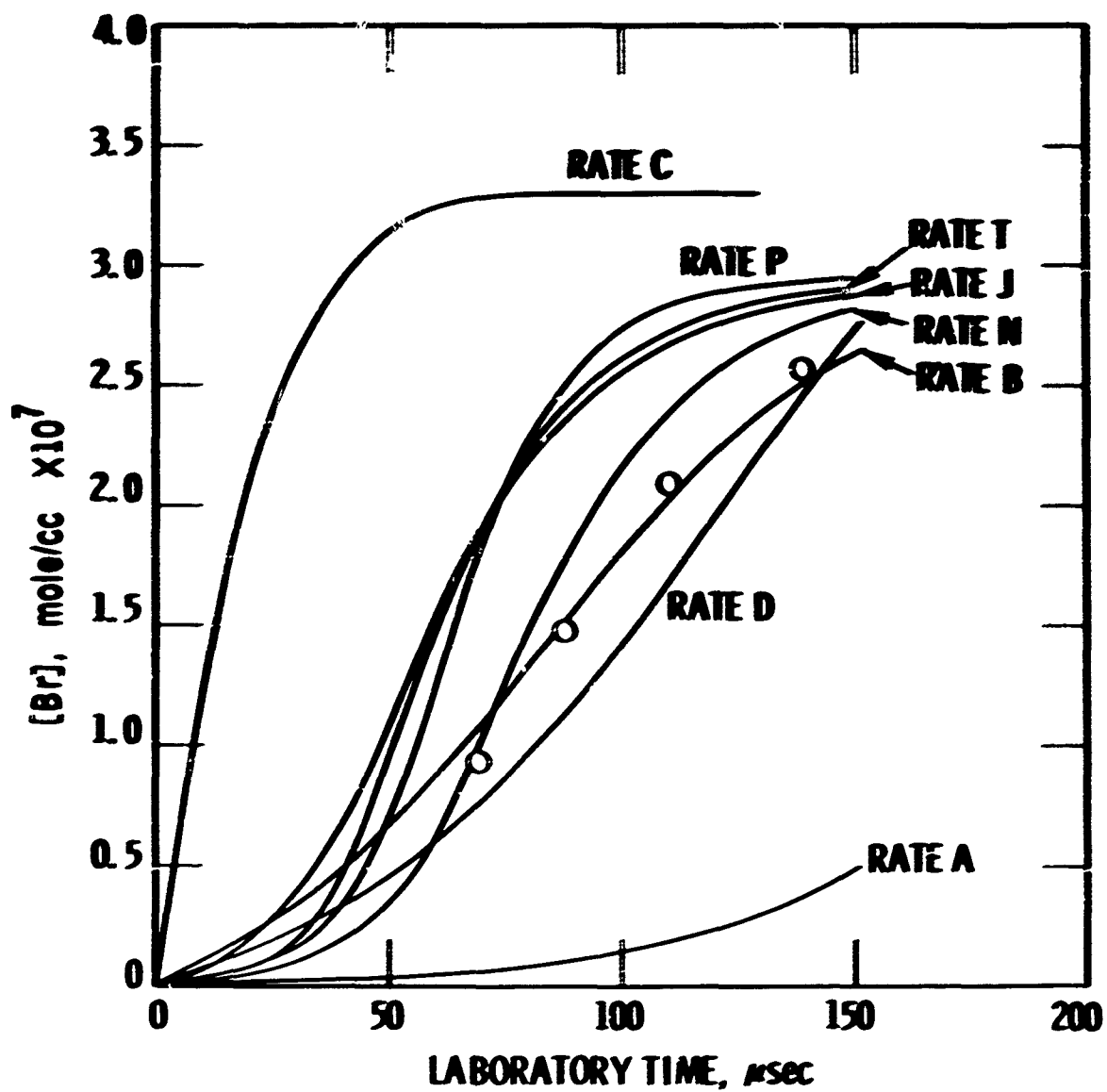


Figure 6. Comparison of Experimental Bromine Profile for Run 26 With Computed Profiles for Various Sets of Rate Coefficients

Table 5. Trial Rate Coefficients

[illegible]

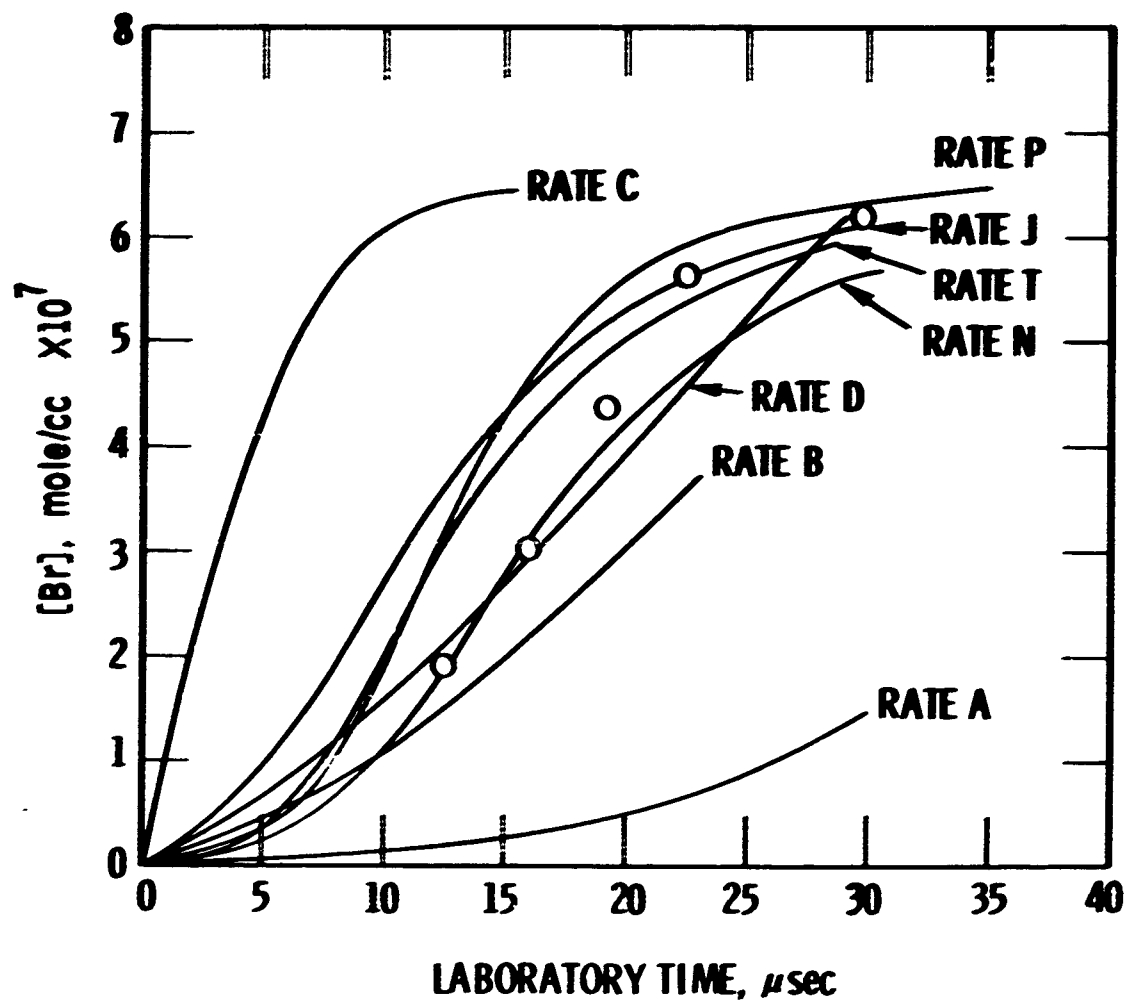


Figure 7. Comparison of Experimental Profile for Run 42 With Computed Profiles for Various Sets of Rate Coefficients

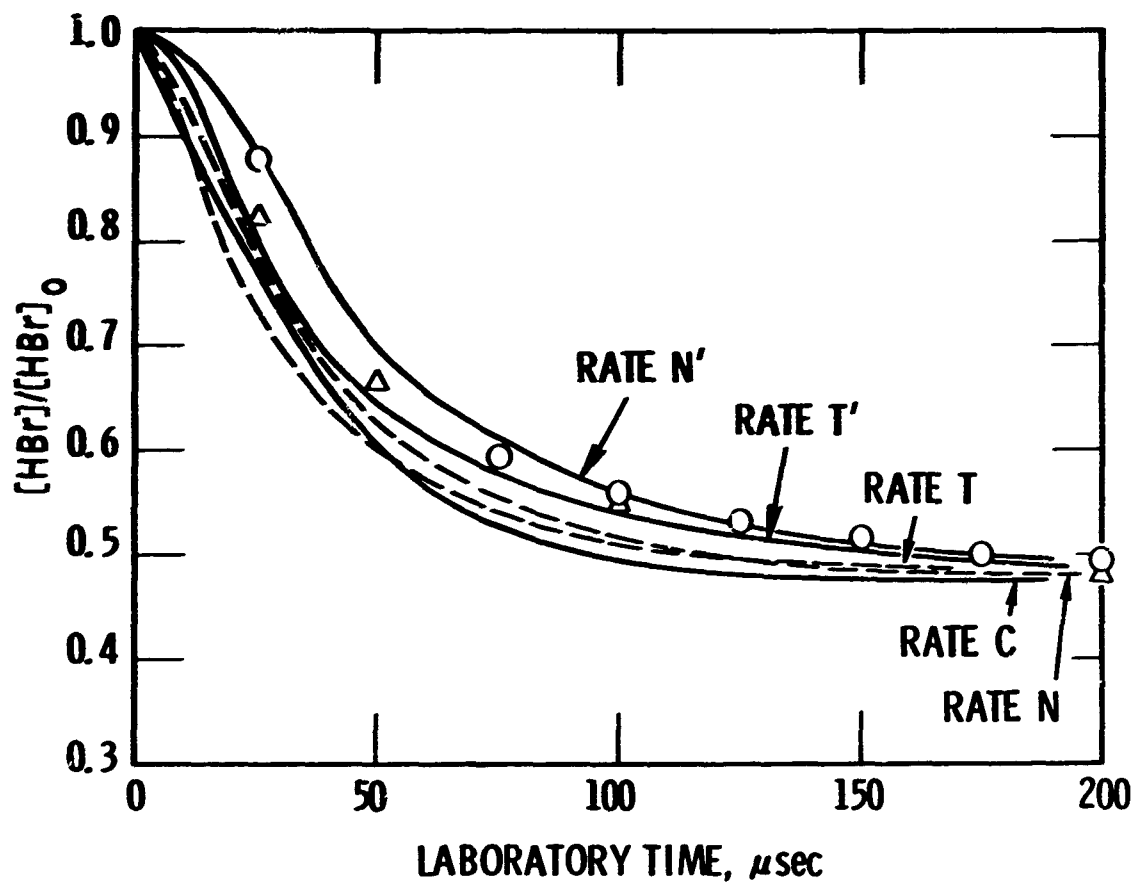


Figure 8. Comparison of Experimental Profile for Run 728 of Ref. 1 With Computed Profiles for Various Sets of Rate Coefficients

k_{-3} by a factor of 2 (rate T, Table 5). Either change reduced the fit somewhat in the 1700-2000°K range. The change in rate T gave a set of rate coefficients that fitted fairly well throughout the entire temperature range of the experiments as well as the temperature range of our earlier work [1]. However, as indicated in Section V, such a large value for k_{-3} is about 30% larger than the probable upper limit of uncertainty as based on the results of previous workers. Nevertheless, we believe that a value of k_{-3} larger than the previous "best estimate" may be appropriate.

Another possible way to fit the low temperature data would be to lower the activation energy for k_1 by a few kcal/mole. An alternative explanation for the recalcitrance of the data below 1550°K could be a systematic error of about 2% in the temperature estimations of the shock-heated gas. Since we cannot guarantee much greater accuracy than this in the temperature measurements, we are reluctant to probe further into the fine details of the various rate coefficients. Westberg and Greene [38] were able to fit their HBr dissociation data (1500-2700°K) with the assumption that $k_1^{\text{HBr}}/k_1^{\text{Ar}} = 1$ and $k_4^{\text{Ar}} = 3$. Their value for k_{-3} closely approximates the value of rate T, i.e., about two times the value of rate N. In other respects, their conclusions agree with those given here. Our value for k_1^{HBr} is almost four times larger than theirs, our k_4^{HBr} is about one-third as large as theirs, and our k_3 is the same as or one-half as large as theirs.

The coefficients of rates T and N were then applied to several runs from our earlier work [1] to determine if they would fit the data in the temperature range of 2400-3800°K. In all but one case, the fit was reasonably good, but could be improved by decreasing k_1^{Ar} by a factor of 4. Figures 8 and 9 show two of the high-temperature experimental profiles and the computer curves generated by rates C, N, T, N', and T'. N' and T' differ from N and T by the values of k_1^{Ar} :

	<u>N and T</u>	<u>N' and T'</u>
$k_1^{\text{Ar}}:$	$10^{22.08} T^{-2} 10^{-88/\theta}$	$10^{21.48} T^{-2} 10^{-88/\theta}$
$k_1^{\text{HBr}}/k_1^{\text{Ar}}:$	3.75	15

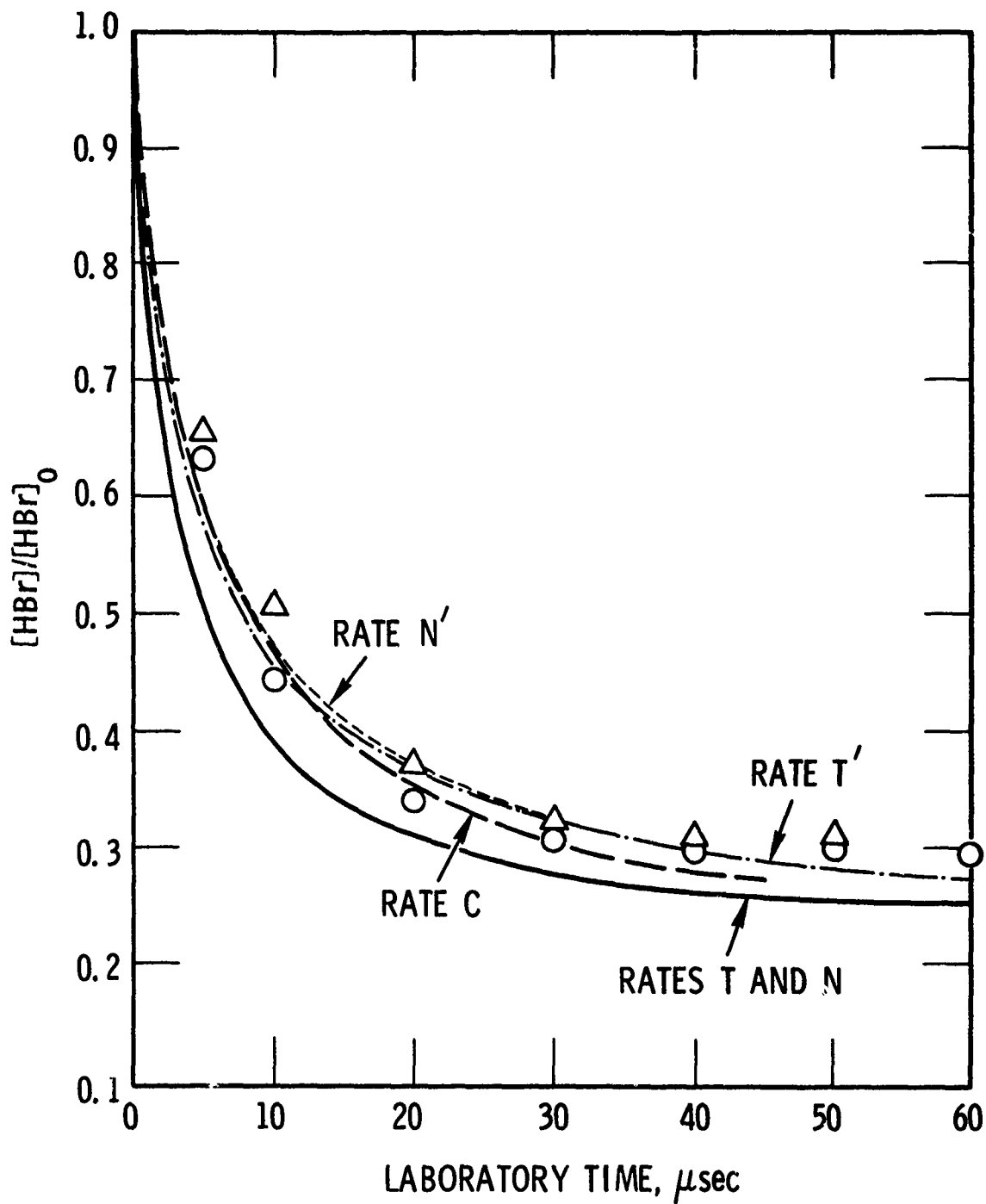


Figure 9. Comparison of Experimental Profile for Run 716 of Ref. 1 With Computed Profiles for Various Sets of Rate Coefficients

s shown in the figures, the sensitivity of the computed profiles to this variation of a factor of 4 is not great. Thus, we conclude that the best value for k_1^{Ar} is $10^{21.78 \pm 0.3} T^{-2} 10^{-88/\theta}$ cc/mole-sec.

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