

THE HYDROGEN-BROMINE REACTION

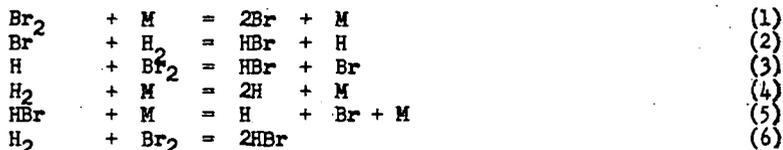
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INTRODUCTION

The reaction between H_2 and Br_2 is the classic example of a chain reaction. It has been studied here by shock wave techniques both to extend the temperature range over which the rate constants have been determined experimentally and to further test the shock tube method. This reaction has been well reviewed, for example by Pease¹ and by Campbell and Fristrom,² and only those pieces of earlier work which are of specific interest will be mentioned below.

The simple reactions which can occur in the hydrogen-bromine system are



(The following notation will be used: K_1 is the equilibrium constant for reaction (1) as written; k_{1f} is the rate constant for the forward reaction in equation (1); k_{1r} is the rate constant for the reverse reaction. All concentrations will be expressed in moles/liter and all times in seconds unless otherwise noted. The units of the equilibrium and rate constants will be the appropriate combinations of moles/liter and seconds.) If reactions (2) and (3) are regarded as the important propagation reactions and it is assumed that the steady state approximation can be applied to the H atom concentration then

$$\frac{d(HBr)}{dt} = (Br) \frac{2k_{2f}k_{3f}(H_2)(Br_2) - 2k_{2r}k_{3r}(HBr)^2}{k_{3f}(Br_2) + k_{2r}(HBr)} \quad (7)$$

Reaction (1) is the source of the bromine atoms. Reactions (4), (5), and (6) are not fast enough to be important and are included in the list for the sake of completeness. At low temperatures or at large relative H_2 and Br_2 concentrations the reverse reaction can be ignored and equation (7) can be rearranged to

$$\frac{d(HBr)}{dt} = \frac{2k_{2f}(Br)(H_2)}{1 + \frac{k_{2r}(HBr)}{k_{3f}(Br_2)}} \quad (8)$$

At low temperatures the Br atoms maintain equilibrium with the molecules and $(Br) = K_1(Br_2)^{1/2}$.

If the correct assumptions are made that reaction (1) can be either ignored or studied independently and that all of the equilibrium constants for the various reactions are known, then two kinetic constants need to be determined to characterize the entire reaction. These two constants have generally been k_{2f} (or $k_{2f}K_1^{1/2}$) and the ratio k_{3f}/k_{2r} .

In the earliest work on this reaction Bodenstein and Lind³ found k_{3f}/k_{2r} to be 10

+ 3. Their values of k_{2f} along with those of Bach, Bonhoeffer, and Molwyn-Hughes⁴ ^{94.} have been recalculated using modern equilibrium constants⁵ and are included in Table V in the discussion. Later Bodenstein and Jung⁶ redetermined k_{3f}/k_{2r} and found it to be 8.4 ± 0.6 . In both cases it was found to be temperature independent.

There have been three studies of this reaction at high temperatures. Britton and Davidson,⁷ in shock tube experiments around 1500°K found that the values of k_{2f} extrapolated from the low temperature values seemed to be low by a factor of about two. They did only a few experiments of a preliminary nature. Plooster and Garvin⁸ compressed mixtures of H₂ and Br₂ in a shock tube and measured the induction times for the onset of explosions. The dependence of these times on temperature was reasonably explained on the basis of values of k_{2f} extrapolated from low temperature values, and the assumption that the Br atom concentration increased with time at the high temperatures behind the shock waves, that is, that the steady state approximation did not apply to Br atoms. Levy⁹ studied this reaction in a flow system in which the H₂ and Br₂ were preheated before being mixed together. The steady state approximation was a reasonable one in view of this preheating and the results could be explained in terms of the low temperature mechanism. Values of k_{2f} were measured between 600° and 1500°K. The scatter in these values at high temperature was quite large, but in general the agreement with the low temperature results was good. In the experiments reported here it was hoped to improve the accuracy of the high temperature measurements and to extend the range to higher temperatures.

EXPERIMENTAL

The shock tube, the associated vacuum line, and the observation arrangements have all been described previously.¹⁰ In all of the experiments reported here the Br₂ concentration was followed spectrophotometrically at 5000 Å. Under the experimental conditions emission at this wave length was negligible. Duplicate observations were routinely made at two stations 40 cm. apart.

Reaction mixtures were prepared by adding Br₂, H₂, HBr and argon to a storage bulb and noting the total pressure after each addition. The mixtures were allowed to mix in the bulbs at least 48 hours before being used, to allow complete mixing.

CALCULATIONS

Calculation of an Apparent Rate Constant in the Reaction between H₂ and Br₂. A shock wave was run in a mixture of Ar, Br₂, H₂, and perhaps HBr, and a trace similar to Figure 1 obtained. The bromine disappearance after the shock front is the sum of two effects, first the dissociation of Br₂ according to reaction (1), and second the formation of HBr according to reactions (2) and (3). These two effects were separated in the following way. All of the concentrations were determined as a function of time. The Br₂ concentration could be read directly from the oscilloscope trace. The compression ratio generally could be assumed to be constant after the shock since the endothermic dissociation of Br₂ which tends to increase this ratio was more or less balanced by the exothermic formation of HBr which tends to decrease this ratio. This also meant that the temperature was much more nearly constant than in a shock involving only the dissociation reaction. The Br atom concentration could be obtained by graphical integration of the Br₂ concentration since

$$\frac{d(\text{Br})}{dt} = 2k_{1f}(\text{Br}_2)(M) - 2k_{1r}(\text{Br})^2(M) \quad (9)$$

and in the reactions between H₂ and Br₂ the last term could be ignored. It must always be remembered in observations on a moving shock wave that the time on the oscilloscope trace, τ , and the time that the gas has been heated, t , are related by $dt = \Delta d\tau$ where Δ is the compression ratio in the shock. The HBr concentration follows from a mass balance of the bromine. The H atom concentration can always be assumed to be negligibly small so that the hydrogen molecule concentration also follows from mass balance. From the concentrations as a function of time $d(\text{HBr})/dt$ and therefore $k^* = 2k_{2f}/[1 + k_{2r}(\text{HBr})/k_{3f}(\text{Br}_2)]$ could be calculated at any time. In

the early stages of the reaction, when the Br atom concentration is small, the rate of formation of HBr is small and the uncertainty in k^* is quite large. In the later stages the back reaction is beginning to be important and the errors in estimating the changes in the temperature and density are becoming large. Therefore it was decided to use the value of k^* at 25% disappearance of the Br_2 in each shock as the best value for that shock.

Calculation of the Rate Constant in the Back Reaction, $\text{Br} + \text{HBr}$. -- The calculations in this case are very similar to those for the forward reaction described in the preceding section. A shock wave was passed through a mixture of HBr and Br_2 , and a trace similar to figure 3 obtained. The change in the Br_2 concentration is again the sum of two effects, the dissociation of Br_2 , and the formation of Br_2 from the reaction between HBr and Br. Since both of these reactions are exothermic it is necessary here to correct for the temperature decrease and the density increase that take place as the reaction proceeds. These changes were approximated as being linear with time, which is not correct, but which does not introduce a large error. The Br_2 concentration could be calculated at all times directly from the oscilloscope trace. The Br atom concentration could be calculated from equation (9), this time including the recombination reaction since the reaction between HBr and Br is slower than the dissociation and recombination of Br_2 . A numerical, point by point, integration was performed to give (Br) as a function of time. The H atom concentration and the HBr concentration could be calculated from mass balance. The H_2 concentration was plotted as a function of time and $d(\text{H}_2)/dt$ could be determined from the plot. The calculated concentrations as a function of the apparent time in the shock wave are shown in figure 4 for the shock shown in the upper trace in figure 3.

The rate constant for the back reaction, k_{3r} , could be calculated from the following rearranged form of equation (7)

$$\frac{d(\text{H}_2)}{dt} = \frac{d(\text{H}_2)}{\Delta d\tau} = \frac{k_{3r}(\text{Br}) \left[(\text{HBr}) - K_6(\text{Br}_2)(\text{H}_2)/(\text{HBr}) \right]}{1 + k_{3r}(\text{Br}_2)/k_{2r}(\text{HBr})} \quad (10)$$

The first term in the numerator represents the reaction in question. The second term represents the reverse of this reaction, that is, the reaction which has previously been called the forward reaction. Since at equilibrium only a small fraction of the HBr has disproportionated this second term must be included. The denominator can be estimated from the known value of the ratio k_{3r}/k_{2r} and is not much greater than 1. The rate constant k_{3r} was generally calculated at a point corresponding to about 25% reaction for reasons similar to those given for the forward reaction.

RESULTS

HBr as a Third Body for the Recombination of Br Atoms. Four series of shocks were run to determine the efficiency of HBr as a third body for the recombination of Br atoms. From the initial rise in concentration in the shock waves in essentially pure HBr it was possible to decide that the HBr was vibrationally relaxed at the shock front and that the apparent dissociation rate constants were not complicated by the simultaneous relaxation of the inert gas. Hydrogen bromide is not truly an inert gas since it can and does disproportionate to H_2 and Br_2 , but it does not do this until a reasonable number of Br atoms are present, so that the initial slope of the oscilloscope trace does give the desired dissociation rate constant for Br_2 . Figure 3 shows the initial dissociation of Br_2 as well as the subsequent decomposition of HBr in a typical shock in an HBr- Br_2 mixture. The point of the inertness of the HBr will be covered more fully in the section Direct Observation of the Back Reaction. The results of these experiments are summarized in Table I. The temperature range in the experiments generally ran from about 1400° to about 1700° K, and the final total concentrations were 10^{-3} - 10^{-2} moles/liter. The 1500° point more or less represents the center of the range.

Table I

Recombination Rate Constants for HBr as Third Body from Shocks in Br₂-HBr Mixtures.

% Br ₂	No. of exptl. points	log k _{1r} = A + B/T		k _{1r} at 1500°K (mole ⁻² liter ² sec ⁻¹)
		A	B	
0.48	12	6.964	2317	3.2 x 10 ⁸
1.00	11	6.123	3705	3.9
2.00	24	6.760	2831	4.4
4.41	8	7.024	2399	4.2

There are two ways of looking at these data. The first is to take the average k from all the mixtures as the best value. The other is to regard the trend with mole fraction of Br₂ as real and extrapolate to the limits, one limit for HBr as third body, and the other for Br₂ as third body. In Table II this has been done at 1500 and 1600°K for HBr, and also for Ar¹⁰ for comparison.

Table II

Recombination Rate Constants from Br₂ - HBr and Br₂ - Ar Mixtures.

Inert Gas	Temp.	mean k	extrapolated values of k _{1r}	
			k _{HBr} or k _{Ar}	k _{Br₂}
HBr	1500°K	4.0 x 10 ⁸	3.6 x 10 ⁸	24 x 10 ⁸
	1600	3.1	2.8	21
Ar	1500	3.7	2.6	37
	1600	3.2	2.3	30

Two conclusions may be drawn from Table II. First, HBr is only slightly more efficient than Ar as a third body for the recombination of Br atoms, perhaps 10-30% more. Second, there is further support for the suggestion that at these temperatures Br₂ is closer to 10 times more efficient than Ar rather than 3 times as has been suggested.¹¹ This support is not very strong, but it is consistent with the Ar results within experimental error.

The Forward Reaction, H₂ + Br₂. About one hundred shocks were run in various mixtures of Br₂, H₂, HBr, and Ar. The argon was the principal constituent, and was added in every mixture to serve as a heat capacity buffer, and also in order to provide a third body with known efficiency for the dissociation of Br₂. An apparent rate constant $k^* = k_{2f} / [1 + k_{2r}(\text{HBr})/k_{2f}(\text{Br}_2)]$ was calculated at the point of 25% reaction as described previously. For any particular mixture the values of k* were compared as a function of temperature. For one sample mixture, 1% Br₂ - 1% H₂ - 98% Ar, the experimental points are displayed in figure 5 as log k* versus 1/T. A straight line has been fitted through these points by the method of least squares. The best straight lines, but not the experimental points, for three other mixtures are also shown in the same figure. All of these straight lines are of the form log k* = A + B/T and the values of the parameters are listed in Table III.

Table III

Apparent Rate Constants at 25% Reaction.

Composition of Mixture				$\log k^* = A + B/T$	
% Br ₂	% H ₂	% HBr	% Ar	A	B
1	1	--	98	11.180	4085 + 342
1	1	10	88	10.702	3940 + 592
2	2	--	96	11.323	4379 + 257
2	2	10	86	10.894	4069 + 363

The actual values of k_{2f} and the ratio k_{3f}/k_{2r} were calculated at several temperatures from points taken from the smoothed curves of figure 5. Two independent estimations were made, one by comparing the results of the 1% Br₂ - 1% H₂ shocks with the results of the 1% Br₂ - 1% H₂ - 10% HBr shocks, and the other by comparing the 2% Br₂ - 2% H₂ with the 2% Br₂ - 2% H₂ - 10% HBr. The values obtained are shown in Table IV.

Table IV

Temp. °K	$k_{2f} \times 10^{-8}$ (moles ⁻¹ liter sec ⁻¹)			k_{3f}/k_{2r}			
	from	1% Br ₂	2% avg.	1%	2%	avg.	
1300		1.16	.98	1.07	9.5	12.7	11.1
1500		3.07	2.76	2.92	8.8	12.8	10.8
1700		6.34	5.88	6.11	8.5	8.2	8.4

Some experiments were also done using higher percentages of bromine and some using excess hydrogen. It was found that when more than 5% of the mixture was reacting the flow behind the shock (or at least the Br₂ concentration) was not smooth even at a distance of forty tube diameters from the membrane. The trace for an extreme case of this type of a shock is shown in figure 2.

As can be seen from the experimental points in figure 5 the spread of the points from the line is about ± 0.1 in $\log k^*$. This must be attributed to the limited accuracy of the shock wave technique. There is further uncertainty introduced by the uncertainty in the value to use for the rate constant for Br₂ recombination. If the value of k_{1r} which was used in the calculations is increased by 5% (this would be the case if Br₂ is five times more efficient than Ar as a third body or if HBr is 50% more efficient) the calculated values of k^* and k_{2f} would be decreased by about 10% and the value of the ratio k_{3f}/k_{2r} would be decreased by about 15%. A conservative estimate of the uncertainty in the constants reported in Table IV is that they are all uncertain by at least 25% and that they are more likely to be too large than too small.

Direct Observation of the Back Reaction. — In many of the shocks in the HBr - Br₂ mixtures it was apparent from the oscilloscope traces that equilibrium had been reached at much higher concentrations of Br₂ than would be expected if the only reaction were the dissociation of Br₂. In four of the shocks in the 0.482% Br₂ - 99.5% HBr mixtures the Br₂ concentration clearly went through a minimum. The most striking example of this is shown in figure 3. In these four shocks the rate constant, k_{3r} , for the reaction between HBr and Br was calculated as outlined in the section on calculations. The results from these four experiments are shown in figure 6 (two points from each experiment). The points show an average scatter of about 10% from $k_{3r} = 8.1 \times 10^{11}/2e^{-44500/RT}$ which was fit to them by the method of least squares. These values

of k_{3r} can be combined with the previous values of k_{2r} to obtain an independent estimate of the ratio $k_{3r}/k_{2r} = (k_{3r}/k_{2r})K_6$. When the actual values of k_{3r} are combined with the smoothed values of k_{2r} from Table VII the resulting values of the ratio show no variation with temperature and have an average value of 8.3 ± 0.7 , which can be compared with the value 10.1 ± 1.7 obtained from the measurements of the forward reaction with and without added HBr.

DISCUSSION

The results of the various studies of the value of k_{2r} are collected in Table V where they are given in two forms, first as $\log k_{2r} = A - B/T$ for convenience in calculation, and second as $k_{2r} = CT^{1/2}e^{-\Delta H/RT}$ since this form has some theoretical justification for a bimolecular reaction.

Table V

The Rate Constant, k_{2r} , for the Reaction between Br and H₂.

temp. °K	range	ref.	$\log k_{2r} = A - B/T$		$k_{2r} = CT^{1/2}e^{-\Delta H/RT}$	
			A	B °K	C liter mole ⁻¹ sec ⁻¹	ΔH kcal/mole
Br + H ₂						
500 - 575		5	11.357	4235 ± 46	5.92×10^9	18.8 ± .2
550 - 600		10	10.927	4053 ± 141	2.15	18.0 ± .7
1300 - 1700		this work	11.254	4195 ± 400	3.54	18.3 ± 1.8
500 - 1700		all	11.238	4190 ± 21	3.35	18.3 ± .1

The probable errors would indicate that neither of these two forms is to be preferred over the other on the basis of the experimental data. The agreement between the low temperature results and the high temperature shock wave results is quite good.

The ratio k_{3r}/k_{2r} which was known to be temperature invariant at low temperatures within experimental error has now been shown to be temperature invariant over the temperature range 300 - 1700°K within experimental error. The best low temperature value, 8.4 ± 0.6 is almost exactly the same as the weighted average of the two independent measurements of the ratio at high temperature, 8.3 ± 0.7 and 10.1 ± 1.7 .

The activation energy associated with k_{2r} is 18.3 kcal/mole (Table VIII). The heat of the reaction at 0°K is 16.2 kcal/mole. This means that k_{3r} and k_{2r} must have an identical activation energy of about 2 kcal/mole. If the value of the ratio at high temperature differs from that at low temperatures by 10% the activation energies would differ by about 0.1 kcal/mole. This pair of activation energies is an embarrassing case for any rule which tries to predict the activation energy from the bond energy of the bond being broken since D_{Br_2} (=45 kcal/mole) and K_{HBr} (= 87 kcal/mole) differ by a factor of 2.

ACKNOWLEDGEMENTS

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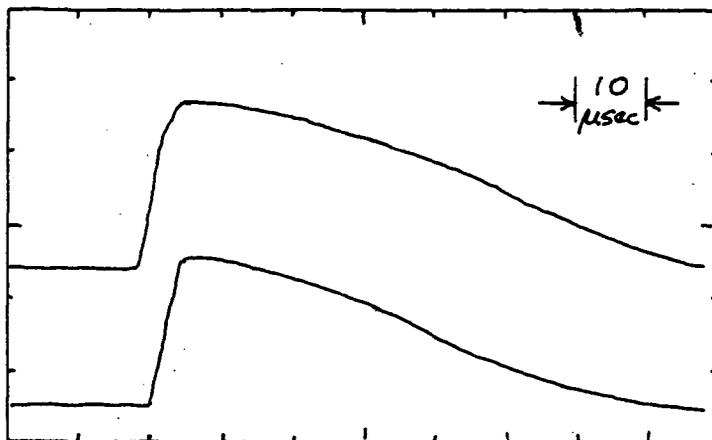


Fig. 1.—Oscillogram of typical shock used for kinetic studies. This shock was run in a 1% H_2 - 1% Br_2 - 98% Ar mixture, and reached a temperature of $1448^\circ K$ at the shock front. Note the acceleration in the rate of disappearance of Br_2 as more Br atoms are produced. (In all of the oscillograms the lower trace records the Br_2 concentration at the first observation station as a function of time, and the upper trace records at the second observation station, 40 cm from the first.)

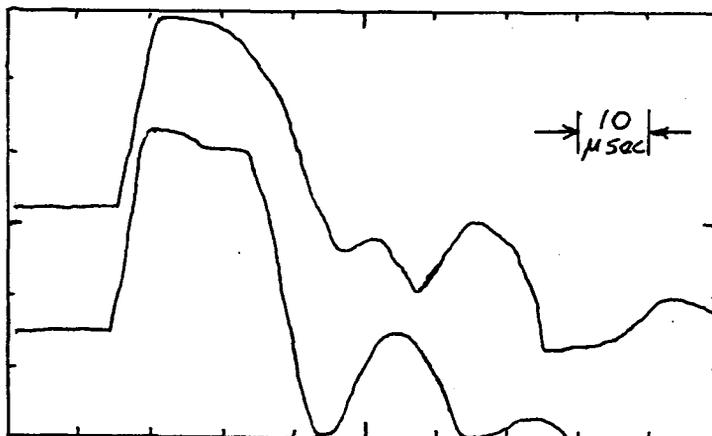


Fig. 2.—Oscillogram of shock in highly exothermic reaction mixture. This shock was run in a 5% Br_2 - 20% H_2 - 75% Ar mixture and reached a temperature of $1424^\circ K$ at the shock front. It is apparent that no useful kinetic data could be obtained in the shocks in concentrated mixtures.

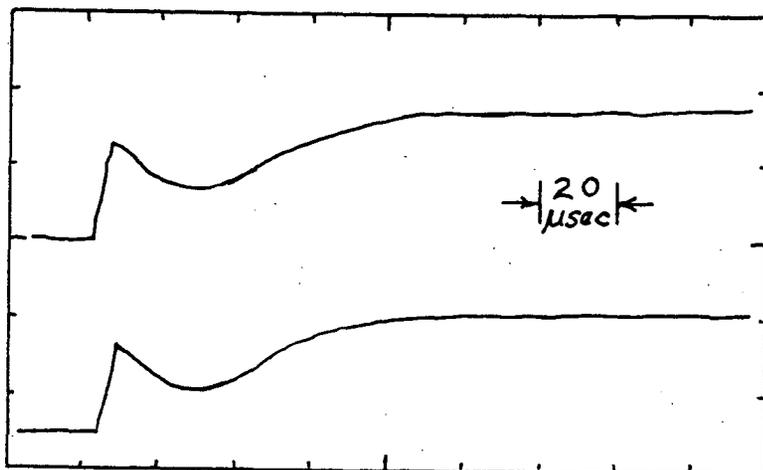


Fig. 3.—Oscilloscope of shock showing the reverse reaction. This shock was run in a 0.5% Br_2 - 99.5% HBr mixture and reached a temperature of 1635°K at the shock front. Note the production of molecular Br_2 when the Br atom concentration becomes sufficiently large.

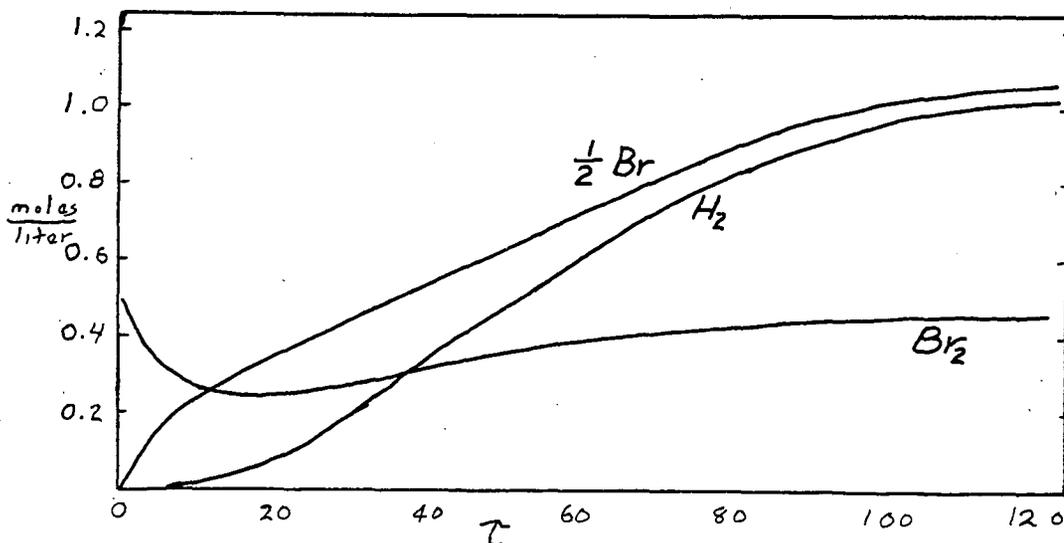


Fig. 4.—Concentrations as a function of time for the upper trace of the shock wave shown in fig. 2. The Br atom concentration is calculated from the known dissociation and recombination rate constants. The H_2 concentration is calculated from mass balance considerations.

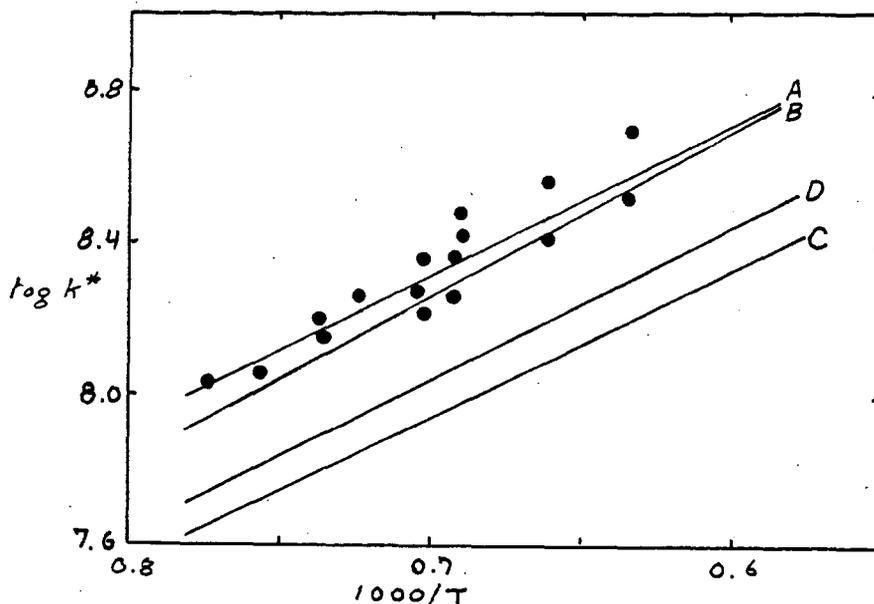


Fig. 5.—Apparent rate constants for the reaction between Br and H₂ at 25% reaction. The points are the experimental points for line A.

A - 1% Br₂ - 1% H₂
 B - 2% Br₂ - 2% H₂

C - 1% Br₂ - 1% H₂ - 10% HBr
 D - 2% Br₂ - 2% H₂ - 10% HBr

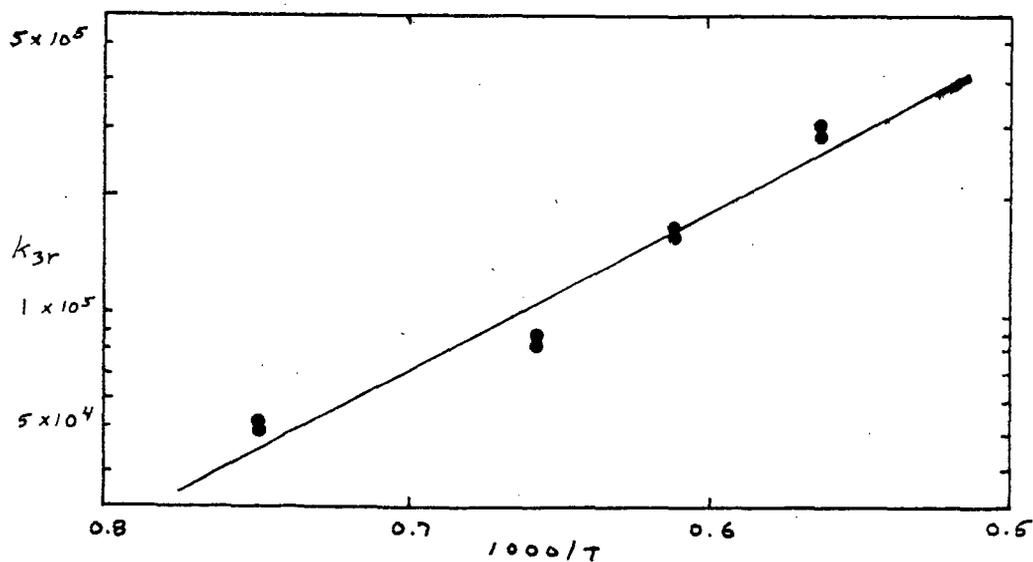


Fig. 6.—Rate constant for the reaction between Br and HBr. The straight line is the least squares line through the points.