REACTION KINETICS, THERMODYNAMICS, AND TRANSPORT IN THE HYDROGEN–BROMINE SYSTEM

A SURVEY OF PROPERTIES FOR FLAME STUDIES

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Received October 8, 1957

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[1] Dr. Campbell's part of this survey was supported in part by the Naval Bureau of Ordnance under contract NORD 15884 with the University of Wisconsin Naval Research Laboratory and by the United States Air Force through the Air Force Office of Scientific Research of the Air Force Research and Development Command, under contract No. AF 49 (638)-169 with New York University. Reproduction in whole or in part is permitted for any purpose of the United States Government.

[2] Dr. Fristrom's part of this survey was supported in part by the Naval Bureau of Ordnance, under contract NOrd 7386. Reproduction in whole or in part is permitted for any purpose of the United States Government.

I. INTRODUCTION

The hydrogen–bromine flame system has been a proving ground for a number of recent theoretical and experimental investigations into the mechanism of flame propagation. There are three reasons for the popularity of this system: (*1*) it is the simplest multicomponent flame system expected to show phenomena typical of complex flames; (*2*) more information is available on the reaction kinetics and general properties of this system than on any other comparable flame; (*3*) since this system can be studied experimentally, theoretical predictions can be tested.

The study of a theoretical model for a flame or the interpretation of any detailed experimental study of a flame system requires information about the chemical reactions occurring and about the thermodynamic and transport properties of each chemical species. The purpose of this review is to compile and to evaluate critically the data required for current theoretical and experimental studies of the hydrogen–bromine system. The listings of *Chemical Abstracts* have been checked up to April 25, 1957. Although more is known about hydrogen–bromine than any other flame, much of the necessary information must be derived from calculations or from empirical interpolations and extrapolations. Therefore, the validity of the methods used to estimate the properties of the individual species and the properties of the mixtures are discussed critically.

If theoretical and experimental studies are to be compared, the limits of significance of the parameters should be known. The effect of varying experimental parameters within the limits of their accuracy gives a necessary test of the sensitivity of a theoretical model. This requires assignment of limits to the uncertainties arising from (*a*) conflicts in data, (*b*) necessary extrapolation of experimental data, and (*c*) estimation of physical properties for which no data are available.

The values of the physical constants recommended in 1952 have been used (62). Since numerical flame studies sometimes require that data be self-consistent and satisfy certain relations, the values given for various parameters in analytic equations for the functions are recorded to ten figures. Those figures which are not significant and have been given to maintain self-consistency are set in italics. If a result is derived from an estimate that can yield at most an order of magnitude, all digits are set in italics. Neither errors that arise from extrapolating data nor errors inherent in approximate formulae were considered in determining which digits to italicize. For purposes of rapid estimation where consistency is not important, graphs of the several functions are given. Each symbol is defined at the point of its introduction. For convenient reference a glossary of symbols is provided in Appendix B.

The thermodynamic properties that are used to obtain parameters in the flame equations are collected and evaluated in Section II, the reaction kinetics in Section III, and the transport properties in Section IV. In each case an attempt has been made to estimate limits of error. Unless otherwise indicated, the limits of error assigned represent the opinions of the authors of this review.

II. THERMODYNAMIC PROPERTIES

The thermodynamic properties of chemical components enter theoretical flame studies in two ways. First, the equilibrium constant is equal to the ratio of the specific rate of the forward reaction to that of the reverse reaction, and second, the enthalpies occur in the energy balance equation. The data required to calculate parameters for analytic expressions for enthalpies and equilibrium constants are reviewed in this section.

A. PARAMETERS USED IN ANALYTIC FORMULAE FOR EQUILIBRIUM CONSTANTS

$K_i(T)$ = equilibrium constant for the i^{th} reaction relative to a standard state of 1 mole cc.$^{-1}$

$(C_v)_\alpha$ = heat capacity at constant volume of a chemical species, α, expressed in units of cal. deg.$^{-1}$ mole^{-1} (1)

$(\overline{C_v})_\alpha$ = value of $(C_v)_\alpha$ averaged over some temperature range of interest

$\Delta_i C_v$ = net change in the $\sum\limits_\alpha (C_v)_\alpha$ due to the i^{th} reaction

$\Delta_i E^\circ(T)$ = standard-state value for change in energy content due to the i^{th} reaction

T_q = a particular T chosen to minimize error in approximate formulae

If the heat capacities are approximated by their average values, the van't Hoff equation for $K_i(T)$,

$$\frac{\mathrm{d}[\ln K_i(T)]}{\mathrm{d}T} = \frac{\Delta_i E^\circ(T)}{RT^2} \tag{2}$$

can be integrated to give the formula:

$$\begin{aligned} K_i(T) &= d_i T^{e_i} \exp\,(-\,\Delta_i E^\circ/RT) && (3)\\ d_i &= K_i(T_q) T_q^{-e_i} \exp\,(\Delta_i E^\circ/RT_q) \\ e_i &= (\Delta_i \overline{C_v})/R \\ \Delta_i E^\circ &= \Delta_i E^\circ(T_q) - T_q \Delta_i \overline{C_v} && (4) \end{aligned}$$

A value for T_q of 1500°K. was selected to minimize the error introduced into flame calculations by using averaged heat capacities in the van't Hoff equation (equation 2).[3]

The formulae used to compute the parameters of equation 3 were:

$$\Delta_i E^\circ(T_q) = \Delta_i E(0^\circ) + \Delta_i[H^\circ(T_q) - H^\circ(0^\circ)] - RT[\Delta_i n]^{3} \tag{5}$$

where $\Delta_i n$ = number of moles of product minus number of moles of reactant for i^{th} reaction

$K_i(T_q)$ = equilibrium constant at temperature T_q with respect to a standard state of 1 mole cc.$^{-1}$

$$K_i(T_q) = (RT_q)^{-\Delta_i n} \exp\,[-\Delta_i F^\circ(T_q)/RT_q] \tag{6}$$

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[3] T_q was chosen as the highest temperature at which all of the relevant data were recorded in 1953 when the calculations were undertaken. Two reasons for this choice are that the maximum flame temperature in some current flame calculations is still higher (1738°K.) and that the important chemical reactions occur in the higher temperature region of the flame. Since that time, data at higher temperatures have been published for bromine (20).

TABLE 1

*Energies of reaction at 0°K.**

i	Reaction i	$\Delta_i E^\circ(0^\circ)$†
1	$Br_2 \rightleftarrows 2Br$	45.428
2	$H_2 \rightleftarrows 2H$	103.253
3	$H_2 + Br \rightleftarrows HBr + H$	16.6925
4	$H + Br_2 \rightleftarrows HBr + Br$	−41.1325
5	$H + Br \rightleftarrows HBr$	−86.5605

* $\Delta_i E^\circ(0^\circ)$ is the standard-state energy change in the units of kilocalories for the i^{th} reaction as written. Where the basic datum was in cm.$^{-1}$, the energy conversion to kilocalories has been made using 1952 physical constants (62).

† Sources of data for the reactions $i = 1, \ldots, 5$:

Reaction 1: Gaydon (27) gives the value 15,890 cm.$^{-1}$

Reaction 2: Herzberg (32) gives the value 36,116 ± 6 cm.$^{-1}$

Reaction 3: $\Delta_3 E^\circ(0^\circ) = \Delta_2 E^\circ(0^\circ) + \Delta_5 E^\circ(0^\circ)$.

Reaction 4: $\Delta_4 E^\circ(0^\circ) = \Delta_1 E^\circ(5^\circ) + \Delta_5 E^\circ(0^\circ)$.

Reaction 5: Herzberg (33) gives the value 3.754 e.v., which is 86.576 kcal. in terms of the 1952 physical constants. His value is based on the National Bureau of Standards Tables, Series III (1948), value for $H_2 + Br_2 = 2HBr$, $\Delta E^\circ(0^\circ) = -24.44$ kcal-mole^{-1}. The value in the above table was recalculated to give exact agreement with this NBS value and the values for $\Delta_1 E^\circ(0^\circ)$ and $\Delta_2 E^\circ(0^\circ)$ which were slightly altered by the newer conversion factors. Herzberg notes that failure to correct for standard states has given an erroneous value in the literature.

$\Delta_i F^\circ(T_q)$ = Gibbs' free-energy change at temperature T_q for the i^{th} reaction with respect to a standard state of the ideal gas at a pressure of 1 atm.

$$\Delta_i F^\circ(T_q) = \sum_\alpha \left\{ T_q \left[\frac{F^\circ_\alpha(T_q) - H^\circ_\alpha(0^\circ)}{T_q} \right] + E^\circ_\alpha(0^\circ) \right\}$$

$E^\circ_\alpha(0^\circ)$ = standard internal energy at absolute zero; the convention is adopted that this is zero when $\alpha = Br_2(g)$ or $\alpha = H_2(g)$

$$\frac{(\overline{C_v})_\alpha}{R} = \left\{ \frac{[H^\circ_\alpha(T_q) - H^\circ_\alpha(0^\circ)] - [H^\circ_\alpha(600^\circ) - H^\circ_\alpha(0^\circ)]}{R(T_q - 600^\circ)} \right\} - 1 \quad \text{[3,4]} \tag{7}$$

The sources of data can be summarized as follows: $\Delta_i E^\circ(0^\circ)$, see the footnote to table 1; for enthalpy and free-energy data, see NBS Tables, Series III, (1948, 1949).[5, 6]

Table 1 lists the $\Delta_i E^\circ(0^\circ)$ and table 2 the energies, free energies, and equilibrium constants evaluated at T_q. The average values of the ratio of the constant-volume heat capacity to the gas constant are given in table 3. The maximum and minimum values for the ratio have also been included in order to show the

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[4] The lower limit of 600°K. was chosen because it was felt that no significant reactions occurred below this temperature.

[5] The discrepancies between data of the National Bureau of Standards and the spectroscopic values of Gordon and Barnes (28) presumably arise from the use by the Bureau of Standards of later values of physical constants. This point has been ignored (48). Although the differences amount to only about 0.03 in $(F^\circ - H^\circ)/T$, this changes appreciably the values of the derived equilibrium constants. The slight discrepancy between the NBS values and Butkov's recalculation of data (16) using later physical constants is probably due to the latter's use of approximate formulae for diatomic molecules. For halogen atoms, the National Bureau of Standards and Butkov are in accord.

[6] Recently, data to higher temperatures have been published for bromine (20).

TABLE 2

*Energies, Gibbs free energies, and equilibrium constants at T_q = 1500°K.**

Reaction i	$\Delta_i E^\circ(T_q)$ †	$\Delta_i F^\circ(T_q)$ ‡	$K_i(T_q)$ §
1. $Br_2 \rightleftarrows 2Br$	$+4.456\mathit{2\ 215} \times 10^{+4}$	$+7.20\mathit{29} \times 10^{+3}$	$+7.2\mathit{50\ 14016\ 8} \times 10^{-7}$
2. $H_2 \rightleftarrows 2H$	$+1.0448\ \mathit{1815} \times 10^{+5}$	$+6.52\mathit{85\ 6} \times 10^{+4}$	$+2.\mathit{499\ 26226\ 6} \times 10^{-15}$
3. $H_2 + Br \rightleftarrows HBr + H$	$+1.702\mathit{0\ 7} \times 10^{+4}$	$+1.385\mathit{8\ 1} \times 10^{+4}$	$+9.5\mathit{69\ 78598\ 5} \times 10^{-3}$
4. $H + Br_2 \rightleftarrows HBr + Br$	$-4.2\mathit{89\ 89} \times 10^{+4}$	$-4.42\mathit{24\ 6} \times 10^{+4}$	$+2.776\ \mathit{11078\ 5} \times 10^{+6}$
5. $H + Br \rightleftarrows HBr$	$-8.746\ \mathit{1115} \times 10^{+4}$	$-5.14\mathit{27\ 5} \times 10^{+4}$	$+3.8\mathit{29\ 04430\ 3} \times 10^{+12}$

* The NBS values have been corrected so that the values for $\Delta_i E^\circ(T_q)$ and $\Delta_i F^\circ(T_q)$ are exactly consistent with the relations between the reactions: 1 + 5 = 4 and 2 + 5 = 3. However, since the exponentials of equation 6 were computed on a ten-digit machine, the values $K_1K_5 = 2.776\ 1107\ 91 \times 10^{+6}$ and $K_2K_5 = 9.569\ 7859\ 41 \times 10^{-3}$ differ in the last two digits from those for K_4 and K_3, respectively.

† $\Delta_i E^\circ(T_q)$ has the units of calories for the reaction as written.

‡ $\Delta_i F^\circ(T_q)$ is the Gibbs free-energy change in the units of calories for the reaction as written. The standard state is the ideal gas at P = 1 atm.

§ $K_i(T_q)$ is the equilibrium constant for the i^{th} reaction with respect to a standard state of 1 mole cc.$^{-1}$ Therefore in equation 6, R = 82.0567 cc. atm. deg.$^{-1}$ mole^{-1}.

TABLE 3

*Heat capacities**

Substance α	$\left[\frac{(C_v)_\alpha}{R}\right]_{\text{min.}}$	$\left[\frac{(C_v)_\alpha}{R}\right]_{\text{max.}}$	$\left[\frac{(\overline{C}_v)_\alpha}{R}\right]$	$\left[\frac{(\overline{C}_v)_\alpha}{R}\right]_{\text{rounded}}$
Br	1.51	1.66	$1.584\mathit{2\ 745}$	1.5
H	1.50	1.50	$1.500\mathit{0\ 000}$	1.5
Br_2	3.48	3.57	$3.5347\ \mathit{115}$	3.5
H_2	2.53	2.88	$2.670\mathit{5\ 655}$	2.5
HBr	2.59	3.18	$2.907\mathit{1\ 363}$	3.0

* The significance of each column is discussed in the last paragraph of the section preceding Section II,B.

range covered by the heat capacity. In order to avoid complicated powers of T in equation 3 for the equilibrium constants, these average values have been rounded to the nearest half-integer for use in flame calculations. Table 6 illustrates the error introduced by rounding. At T = 1700°, which lies in the region of rapid reactions in this flame, the rounding introduces a difference less than a few tenths of 1 per cent. As the temperature decreases and the rounding error increases, the significance of the error for flame calculations is decreased by the progressive decrease in the rate of chemical reactions. The error introduced by using average values probably dominates that of rounding the average values. The parameters in the analytic formulae (equation 3) for $K_i(T)$ are recorded both for $(\Delta_i\overline{C}_v)/R$ and for $[\Delta_i\overline{C}_v)/R]_{\text{rounded}}$ (the former in table 4, the latter in table 5).

B. PARAMETERS IN LINEAR EQUATIONS FOR THE ENTHALPIES

The convention

$$H^\circ_{Br_2}(0^\circ) = H^\circ_{H_2}(0^\circ) = 0 \tag{8}$$

was adopted as a reference point for calculating heat contents. Then the enthalpies were approximated as the linear functions of T,

TABLE 4

Parameters for $K_i(T) = d_i T^{e_i} \exp(-\Delta_i E^\circ/RT)$*; based on the* $(\Delta_i \overline{C}_v)/R$

Reaction i	d_i	e_i	$\Delta_i E^\circ$
1	$+4.7310\ 86660 \times 10^{+1}$	$-0.3661\ 625$	$+4.5653\ 66669 \times 10^{+4}$
2	$+2.6991\ 07059 \times 10^{-1}$	$+0.3294\ 345$	$+1.0349\ 98416 \times 10^{+5}$
3	$+8.1458\ 45678 \times 10^{-1}$	$+0.1522\ 963$	$+1.6566\ 73749 \times 10^{+4}$
4	$+1.4278\ 31538 \times 10^{+2}$	$-0.5433\ 007$	$-4.1279\ 43742 \times 10^{+4}$
5	$+3.0179\ 77983 \times 10^{0}$	$-0.1771\ 382$	$-8.6933\ 10411 \times 10^{+4}$

The parameters were computed from equations 3, 4 using the $[\Delta_i \overline{C}_v]/R$. In order to maintain consistency with the relations between the reactions, d_4 was computed as $d_1 d_5$ and d_3 as $d_2 d_5$. The reactions are given the same numbers as in the three preceding tables.

TABLE 5

Parameters for $K_i(T) = d_i T^{e_i} \exp(-\Delta_i E^\circ/RT)$*; based on the* $[(\Delta_i \overline{C}_v)/R]_{\text{rounded}}$

Reaction i	d_i	e_i	$\Delta_i E^\circ$
1	$+1.4393\ 48323 \times 10^{+2}$	-0.50	$+4.6052\ 60750 \times 10^{+4}$
2	$+6.5375\ 17476 \times 10^{-2}$	$+0.50$	$+1.0299\ 14225 \times 10^{+5}$
3	$+4.5247\ 19883 \times 10^{-2}$	$+0.50$	$+1.5530\ 30750 \times 10^{+4}$
4	$+9.9619\ 58801 \times 10^{+1}$	-0.50	$-4.1408\ 59750 \times 10^{+4}$
5	$+6.9211\ 59140 \times 10^{-1}$	0	$-8.7461\ 11500 \times 10^{+4}$

The parameters were computed from equations 3, 4, using $[(\Delta_i \overline{C}_v)/R]_{\text{rounded}}$. In order to maintain consistency with the relations between the reactions, d_4 was computed as $d_1 d_5$ and d_3 as $d_2 d_5$.

TABLE 6

Error introduced into $K_i(T)$ *by using rounded average heat capacities*

T	$i = 1$	$i = 2$	$i = 3$	$i = 4$	$i = 5$
500	a: 4.779×10^{-20}	1.406×10^{-45}	1.674×10^{-7}	$5.144 \times 10^{+18}$	$1.172 \times 10^{+38}$
	b: 5.392×10^{-20}	1.205×10^{-45}	1.223×10^{-7}	$4.948 \times 10^{+18}$	$9.990 \times 10^{+37}$
1700	a: 4.193×10^{-6}	1.550×10^{-13}	1.889×10^{-2}	$4.962 \times 10^{+5}$	$1.213 \times 10^{+11}$
	b: 4.197×10^{-6}	1.548×10^{-13}	1.884×10^{-2}	$4.960 \times 10^{+5}$	$1.212 \times 10^{+11}$

a: Values of $K_i(T)$ calculated using $[(\Delta_i \overline{C}_v)/R]_{\text{rounded}}$.
b: Values of $K_i(T)$ calculated using $(\Delta_i \overline{C}_v)/R$.
Note that $T_q = 1500^\circ$ was used to determine the constants in equations 3, 4.

$$H^\circ_\alpha(T) = H^\circ_\alpha(T_r) + (\overline{C}_p)_\alpha(T - T_r) \tag{9}$$

where T_r = a reference temperature and $(\overline{C}_p)_\alpha$ = an average constant-pressure heat capacity of component α; the average constant-volume heat capacities are recorded in table 3.

The $H^\circ_\alpha(T_r)$ values were computed from the equation

$$H^\circ_\alpha(T_r) = [H^\circ_\alpha(T_r) - H^\circ_\alpha(0^\circ)] + E^\circ_\alpha(0^\circ) \tag{10}$$

using tabulations of $[H^\circ_\alpha(T) - H^\circ_\alpha(0^\circ)]$,[7] the convention of equation 8, and the $\Delta_i E^\circ(0^\circ)$ values of table 1. Since in flame calculations the high-temperature region is considered to be the most important, T_r was chosen as 1738°, the maximum temperature in a flame studied by one of the authors. The values are recorded in table 7.

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[7] See the note to table 7 for the sources of data.

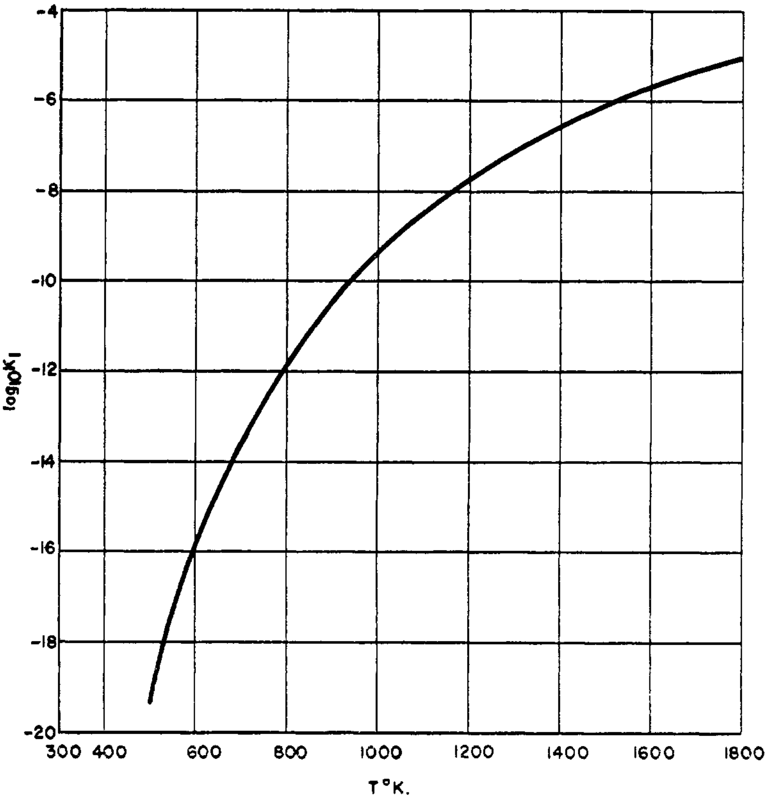

FIG. 1. Log of the equilibrium constant for the reaction $Br_2 \rightleftarrows 2Br$ with respect to a standard state of 1 mole cc.$^{-1}$; *cf.* table 5.

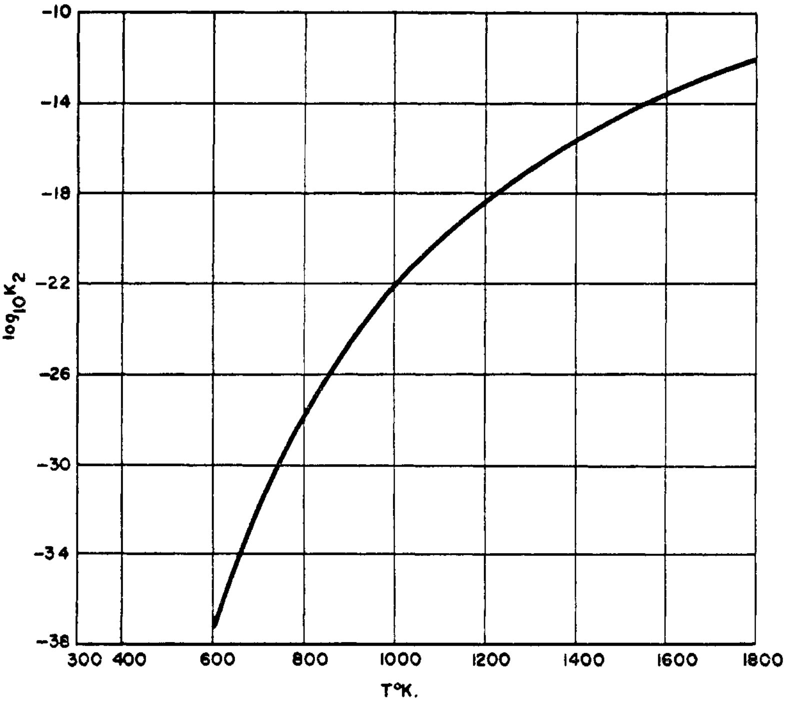

FIG. 2. Log of the equilibrium constant for the reaction $H_2 \rightleftarrows 2H$ with respect to a standard state of 1 mole cc.$^{-1}$; *cf.* table 5.

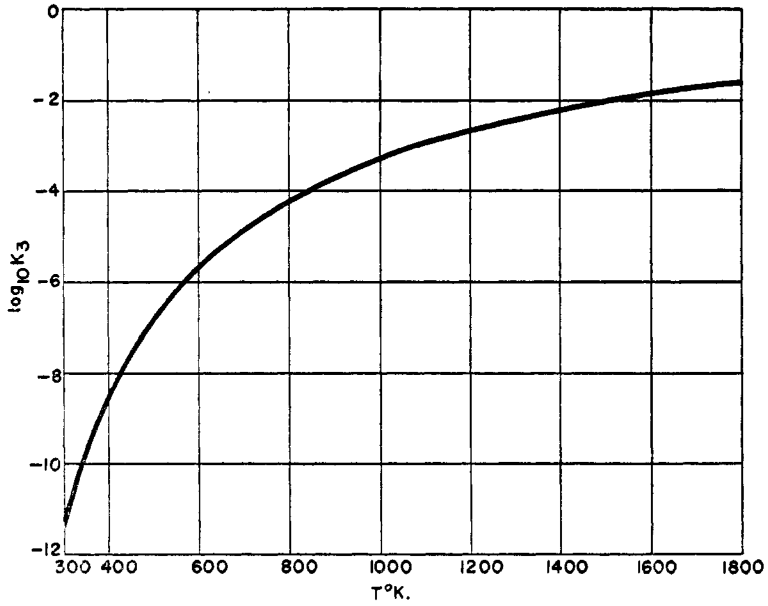

FIG. 3. Log of the equilibrium constant for the reaction $H_2 + Br \rightleftarrows HBr + H$ with respect to a standard state of 1 mole cc.$^{-1}$; *cf.* table 5.

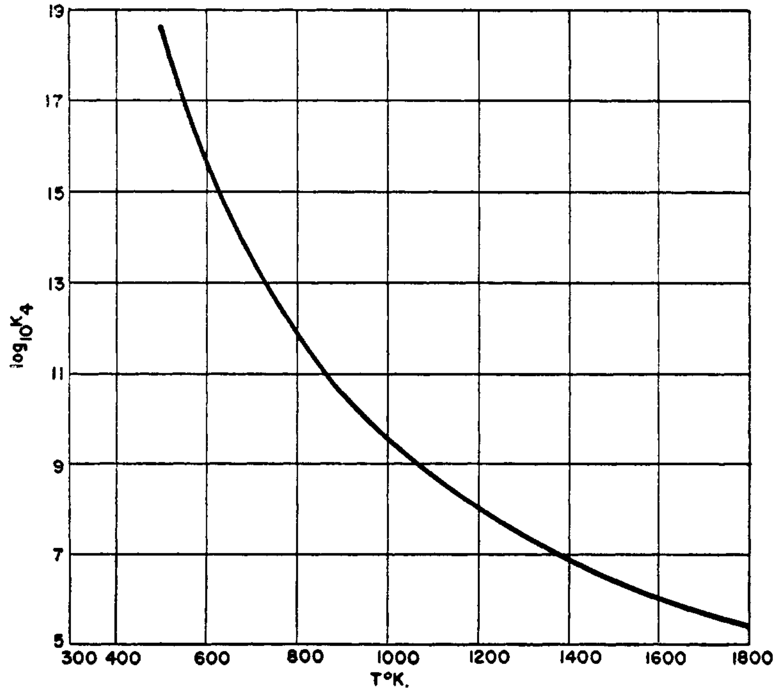

FIG. 4. Log of the equilibrium constant for the reaction $Br_2 + H \rightleftarrows HBr + Br$ with respect to a standard state of 1 mole cc.$^{-1}$; *cf.* table 5.

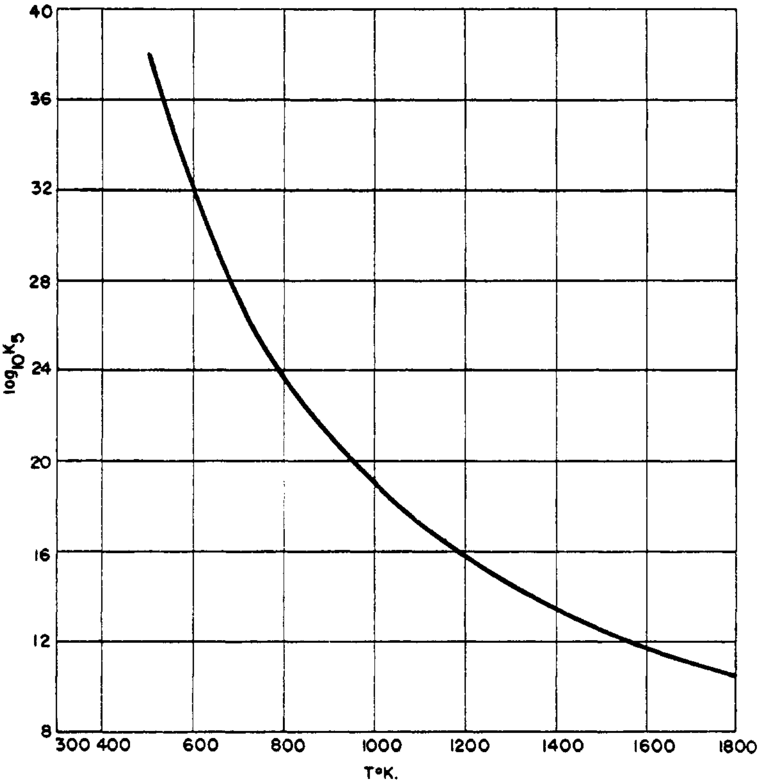

FIG. 5. Log of the equilibrium constant for the reaction H + Br $\rightleftarrows$ HBr with respect to a standard state of 1 mole cc.$^{-1}$; *cf.* table 5.

III. REACTION KINETICS

A. FUNCTIONAL FORM ASSUMED FOR SPECIFIC RATE CONSTANTS; RELATION BETWEEN THE CONSTANTS FOR FORWARD AND REVERSE REACTIONS

This section reviews ideas about specific rate constants which are used in interpreting recent work on bromine dissociation and which form the basis for choosing the functional form for the constants.

The conventional theory of the specific rate constant (23, 24) poses two fundamental problems: (*a*) What conditions, energetic or other, must be satisfied if the reaction is to occur, and (*b*) how often are these conditions met? Since no basis for predicting the conditions is known, one must assume a model and test it for agreement with experimental rate data. One common hypothesis is that (*a*) the conditions demand certain types of collisions between molecules, and (*b*) these special collisions occur with a frequency predicted by equilibrium theory. The equilibrium method of calculating frequency depends on the hypothesis that the processes (average molecules $\leftrightarrows$ energetic molecules) are so much faster than the process (energetic molecules $\rightarrow$ reaction products) that energetic molecules remain in approximate equilibrium with average molecules of reactant.

TABLE 7

Enthalpies at 1738°K.

Substance α	$H_\alpha^\circ(T_r)$	Substance α	$H_\alpha^\circ(T_r)$
	cal./mole		*cal./mole*
Br	$+3.1951\ 951 \times 10^{+4}$	H_2	$+1.2558\ 694 \times 10^{+4}$
H	$+6.0260\ 884 \times 10^{+4}$	HBr	$+8.4580\ 488 \times 10^{+2}$
Br_2	$+1.5254\ 478 \times 10^{+4}$		

The $H_\alpha^\circ(T_r)$ were computed from equation 10. For Br and Br_2 the values were interpolated from data in reference 20; for H and H_2, from data in NBS Tables, Series III. $[\overset{\circ}{H}_{HBr}\ (1500^\circ) - \overset{\circ}{H}_{HBr}\ (0^\circ)]$ was obtained from the NBS Tables, and $\overset{\circ}{H}_{HBr}(T_r) - \overset{\circ}{H}_{HBr}\ (1500^\circ)$ was estimated by extrapolation. Past flame calculations have used the following values computed in the same way as that for hydrogen bromide:

$Br = 3.1499\ 878 \times 10^{+4}$; $H = 6.0260\ 778 \times 10^{+4}$

$Br_2 = 1.5220\ 280 \times 10^{+4}$; $H_2 = 1.2349\ 529 \times 10^{+4}$

Several possible models predict that a specific rate constant, $k(T)$, will have the functional form,

$$k(T) = gT^h \exp(-\Delta E/RT) \tag{11}$$

where g and h are constants. For example, suppose that: (*1*) classical mechanics is adequate; (*2*) the reaction requires the collision of two molecules; (*3*) the collision leads to reaction if and only if it provides a minimum energy, E^*; and (*4*) Z is the total number of collisions per unit volume per unit time

$$Z = \frac{2\nu_1 \nu_2}{s_{12}} r_{12}^2 \left(\frac{2\pi kT}{\mu}\right)^{\frac{1}{2}} \tag{12a}$$

where ν_1, ν_2 = number of molecules per unit volume of types 1 and 2
s_{12} = a symmetry number which is 1 if the two molecules are different and 2 if they are the same (12b)
r_{12} = the collision diameter
μ = the reduced mass = $M_1M_2/(M_1 + M_2)$

Then,

1. If the energy of relative motion must exceed E^* at the time of impact and if $E^* \gg kT$,

$$k(T) \simeq Z(E^*/kT) \exp(-E^*/kT) \tag{13}$$

2. If the energy of relative motion along the line of centers must exceed E^* at the time of impact,

$$k(T) = Z \exp(-E^*/kT) \tag{14}$$

3. If there are s vibrations which can be approximated as harmonic oscillators for which $h\nu \ll kT$, if there are R classical rotations, if the sum of the energy of relative motion along the line of centers plus the energy of the s vibrations and the R rotations must exceed E^* at the time of impact, and if $E^* \ll [(R/2) + s]kT$, then

$$k(T) \simeq \{Z(E^*/kT)^{[(s/2)+R]} \exp(E^*/kT)\}/\Gamma[(R/2) + s + 1] \tag{15}$$

$\Gamma(Z)$ = the gamma function, which equals $(Z - 1)!$ when Z is a positive integer.

Equation 11 was adopted as the functional form for each of the specific rates since it was predicted by these simple models. Unfortunately, even when rate data exist, they are usually so inaccurate that a variation of h by as much as an integer will not significantly affect the agreement between calculated and experimental data.

Whenever the rate law for the reaction in one direction was known, that for the other direction was obtained from the thermodynamic equation

$$K_i(T) = k_i^f(T)/k_i^r(T) \tag{16}$$

where $K_i(T)$ = equilibrium constant for the i^{th} reaction, with respect to a standard state of an ideal gas at a concentration of 1 mole cc.$^{-1}$

B. CONVENTIONAL MECHANISM FOR THE HYDROGEN–BROMINE REACTION

The following empirical rate law governs the kinetics over the approximate temperature range 0–300°C.:[8, 9]

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \frac{k'_{\text{exp}}(a - x)\sqrt{b - x}}{4.2 + \dfrac{x}{b - x}} \tag{17}$$

where a = initial concentration of H_2 in moles/cc.
b = initial concentration of Br_2 in moles/cc.
x = decrease in the concentration of H_2 or of Br_2

This law is consistent with the following assumptions:

1. Because of the high activation energies for some of the other possible reactions and because of the low free-radical concentrations, the only significant reactions in this temperature range are:[10, 11]

$$\begin{aligned} Br_2 &\underset{k_1^r}{\overset{k_1^f}{\rightleftarrows}} 2Br \\ Br + H_2 &\underset{k_3^r}{\overset{k_3^f}{\rightleftarrows}} HBr + H \\ H + Br_2 &\xrightarrow{k_4^f} HBr + Br \end{aligned} \tag{18}$$

2. Under the experimental conditions both H and Br obey steady-state approximations. The approximation for H,

$$\frac{\mathrm{d}[H]}{\mathrm{d}t} \cong 0 \tag{19}$$

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[8] For a review of experimental data and its interpretation, see Kassel (44) and Pease (56). Note that on p. 119 Pease gives the newer value, 4.2, for the constant in equation 17; elsewhere he uses the older value, 5.

[9] Equation 17 is written in Pease's notation (56; *cf.* pp. 115 and 120).

[10] For a discussion of this choice of reactions, see Frost and Pearson (26).

[11] The notation used for the specific rate constants is that adopted in Section III,C of this review.

reduces the steady-state approximation for Br to the assumption that bromine atoms are in equilibrium with bromine molecules:

$$[Br_2] \cong K_1(T)[Br]^2 \tag{20}$$

C. MECHANISM USED IN CURRENT FLAME STUDIES

When the theoretical study of hydrogen–bromine flames was begun, it was necessary to ask whether other reactions in addition to those considered in the conventional mechanism might become important at the higher temperatures of flames. Moreover, the applicability of the steady-state approximations was uncertain. Benson (10) had considered the validity of the steady-state approximation for several simple types of mechanisms and discussed a chain reaction of the hydrogen–bromine type.[12] His approximate treatment suggested that the steady state should be valid for Br at ordinary, but not necessarily at higher, temperatures.[13] Even if the steady-state approximations were valid for both H and Br in a flame, it would be important to establish this validity rather than introduce it as an *ad hoc* assumption. The accuracy of the steady-state approximation will have an important effect upon the role of diffusion of free radicals and the significance of this diffusion lies at the heart of the basic controversy over what is important in establishing a steady-state flame. After consideration of other possible reactions, the following more general model consisting of five homogeneous gas reactions was assumed.

$$\left.\begin{array}{l}(1)\ X^* + Br_2 \rightleftarrows 2Br + X\\(2)\ X^* + H_2 \rightleftarrows 2H + X\\(3)\ Br + H_2 \rightleftarrows HBr + H\\(4)\ H + Br_2 \rightleftarrows HBr + Br\\(5)\ X + H + Br \rightleftarrows HBr + X^*\end{array}\right\} \tag{21}$$

where X = any of the constituents of the gas mixture and $k_i^f(T)$, $k_i^r(T)$ = specific rate constant for the i^{th} reaction in the forward and reverse directions, respectively.

All concentrations are in the units of moles per cubic centimeter. In reactions 1, 2, 5 the rates are taken with respect to the atom concentrations. For example, in reaction 1

$$d[Br]/dt = k_1^f[Br_2] - k_1^r[Br]^2$$

Note that there are two relations between the equilibrium constants for reactions 1 to 5:

$$K_1(T)K_5(T) = K_4(T), \text{ and } K_2(T)K_5(T) = K_3(T) \tag{22}$$

Probably the most serious limitation in this list of reactions is the neglect of a possible bimolecular reaction such as the one which dominates the hydrogen–

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[12] See Benson (10, Section IV, p. 1610).

[13] Professor Benson discussed its questionable validity at elevated temperatures in a private communication.

TABLE 8

Significance of reaction 4 reverse

T	R_4^r/R_4^f*	T	R_4^r/R_4^f*
°K.		°K.	
1738	1.0	1648	0.044
1732	0.56	1565	0.015
1712	0.19		

* R_4^r/R_4^f is the ratio for the rates of reaction 4 reverse to reaction 4 forward in one theoretical model for an equimolar hydrogen-bromine flame with a flame-holder temperature of 373°K.

iodine reaction at ordinary temperatures. Estimates of the probable rate indicated that this reaction should be less important than reactions 3, 4. This point and the neglect of a possible Br_3 intermediate for the recombination of bromine atoms is discussed in Appendix A.

Preliminary results from the numerical integration of the flame equations for an equimolar mixture of hydrogen and bromine provide a basis for a tentative discussion of the relative importance of the reactions (17).[14] Since the temperature should play a significant role in determining the character of the reaction, it is important to note that the maximum temperature for this flame is estimated as 1738°K. When the parameter values assigned in this review are used, the results agree with the conventional mechanism in the following respects: reactions 3, forward and reverse, and reaction 4 forward are of great and about equal importance:

$$(3)\quad H_2 + Br \rightleftarrows HBr + H$$
$$(4)\quad Br_2 + H \rightleftarrows HBr + Br$$

Moreover, H appears to obey the steady-state approximation, in general, to within 1 per cent through the temperature range where significant chemical reaction occurs, and the contribution of the dissociation and recombination of hydrogen (i.e., reaction 2) is less than 1/1000th the actual rate of production of H. Reaction 5, $X + H + Br \rightleftarrows HBr + X$, is of secondary importance since it contributes about 1 per cent to the rate of formation of Br in the high-temperature region. However, the results differ from the conventional mechanism in two respects: (*a*) table 8 shows that reaction 4 reverse makes a contribution comparable to that of reaction 4 forward at high temperatures, and (*b*) the steady-state approximation for Br is completely inadequate and leads to an error in the mole fraction of Br of about 70 per cent at the maximum Br concentration.

D. PARAMETERS FOR SPECIFIC RATE CONSTANTS

The following subsections (III,D,1 to III,D,3) are devoted to the evaluation and use of experimental data to compute the parameters in equation 11 for the specific rate constants. For convenient reference the resulting values are tabulated in Section III,D,4, and graphs are provided in Section III,E for rapid but rough estimates of their values.

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[14] These results are subject to theoretical limitations discussed in the article.

1. Parameters for reaction 3: $\mathrm{Br} + \mathrm{H_2} \rightleftarrows \mathrm{HBr} + \mathrm{H}$

The conventional mechanism discussed in Section III,B can be shown to imply that

$$\frac{\mathrm{d[HBr]}}{\mathrm{d}t} = \frac{[(2k_4^f\,k_3^f\,\sqrt{K_1})/k_3^r][\mathrm{H_2}][\mathrm{Br_2}]^{\frac{1}{2}}}{(k_4^f/k_3^r) + ([\mathrm{HBr}]/[\mathrm{Br_2}])} \tag{23}$$

Comparison with equation 17 and use of the relation

$$2x = [\mathrm{HBr}] \tag{24}$$

shows that

$$k'_{\mathrm{exp}} = (k_3^f\sqrt{K_1})(k_4^f/2k_3^r) \tag{25}$$

$$k_4^f/2k_3^r = 4.2 \tag{26}$$

Actually Bodenstein and Jung (11) found $k_4^f/2k_3^r$ to be 4.3 at 30°C. and 4.1 at 302°C. The difference between these two values lay within their experimental error. Over this temperature range, the ratio therefore appears to be constant with a possible variation of perhaps 10 per cent.

As the first step in determining the parameters for $k_3^f(T)$, the experimental values for k_3^f were computed from equations 25 and 26, using k'_{exp} and values of $K_1(T)$ interpolated from data of the National Bureau of Standards.[15] Next, approximate empirical activation energies were taken from the slope of the plot of T^{-1} versus

$$\ln k_3^f - h_3^f \ln T \tag{27}$$

Despite the fact that the models discussed in Section III,A predict $h_3^f \leqslant +\frac{1}{2}$ the values $h_3^f = -\frac{1}{2}, 0, +\frac{1}{2}, +1, +\frac{3}{2}$ were all tried. When the ratio

$$g_3^f = k_3^f/[T^{h_3^f}\exp(-\Delta E_3^f/RT)] \tag{28}$$

was computed using experimental values for k_3^f, it was found that the variation in g_3^f was relatively insensitive to the choice of h_3^f. The experimental datum at 574.4°C. was ignored, since in every case it gave great deviation. For the remaining experimental points the average deviation from the mean g_3^f varied from 6.7 per cent for $h_3^f = 0$, to 4.7 per cent for $h_3^f = 1$. Even this slight difference was due at least in part to the estimate of the best slope for each value of h_3^f. Therefore, $h_3^f = 1$ was chosen arbitrarily, and the value of ΔE_3^f was adjusted numerically by trial and error until all trend with temperature in the sign of deviations of g_3^f from its mean value disappeared.

This process gave

$$g_3^f = +3.46 \times 10^{+10},\ h_3^f = +1,\ \Delta E_3^f = +1.664 \times 10^{+4} \tag{29}$$

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[15] Either Bessel's or Stirling's formula, depending upon the range in which interpolation was required, was used to calculate $[F^\circ - H^\circ(0^\circ)/T]$ from National Bureau of Standards Tables, Series III (1948). $\Delta_i E^\circ(0^\circ)$ from table 1 then gave $\Delta_i F^\circ$. $K_i(T)$ was computed using equation 6.

TABLE 9

Data for computing parameters for $k_3^f(T)$; comparison with experiment

T	k'_{exp} *	K_1 †	k_3^f ‡	k_3^f §	Per Cent Deviation¶
°*A*.					
498.8	8.08×10^{-4}	4.9168×10^{-20}	8.68×10^{5}	8.84×10^{5}	+1.84
524.5	6.48×10^{-3}	4.6153×10^{-19}	2.27×10^{6}	2.12×10^{6}	−6.61
549.0	3.14×10^{-2}	3.2072×10^{-18}	4.17×10^{6}	4.51×10^{6}	+8.15
550.6	3.97×10^{-2}	3.6205×10^{-18}	4.97×10^{6}	4.73×10^{6}	−4.83
574.4	2.13×10^{-1}	2.0083×10^{-17}	1.132×10^{7}	9.27×10^{6}	−18.11
585.5	3.37×10^{-1}	4.2567×10^{-17}	1.23×10^{7}	1.25×10^{7}	+1.63
612.1	1.52×10^{0}	2.3040×10^{-16}	2.38×10^{7}	2.42×10^{7}	+1.68

* For the definition of k'_{exp} see equation 17. The numerical values were taken from Pease (56).

† K_1 is an equilibrium constant for a standard state of an ideal gas at a concentration of 1 mole cc.$^{-1}$

‡ These values were computed from experimental data by solving equations 25 and 26.

§ These were calculated using the parameter values given by equation 29.

¶ The average per cent deviation of the calculated from the experimental values is 6.1 per cent; excluding the point at T = 574.4°A., the average is 4.1 per cent.

Table 9 gives some of the data used to compute these parameters and a comparison of the results with experiments.

As will be shown in Section III,D,4, there is no reason to suppose that the parameters of equation 29 which have been derived from empirically fitting data from 499 to 612°K. will represent data at flame temperatures over a thousand degrees higher. Recently, shock waves have been used to obtain preliminary results on the high-temperature hydrogen–bromine reaction (14).[16]

The rate of disappearance of bromine under the experimental conditions was calculated by equating the observed rate to the sum of the rates due to the dissociation of bromine and due to the chain steps 3 and 4 forward. Since Section III,D,3 shows that the estimate of the rate of dissociation of bromine is subject to considerable uncertainty, and since in the shock-wave experiments this contribution was about the same size as that of reaction 3 forward, the estimate of k_3^f is subject to similar uncertainty. Table 10 compares the experimental estimates with values calculated using an empirical equation quoted by Pease (56) and with values calculated using the parameters of equation 29.

Britton and Davidson felt that their shock-wave results offered some evidence that the Pease empirical equation would give considerable error in extrapolation, but that the results were too tentative to use in revising the equation. The equation proposed in this review is nearer the range of shock-wave values at both low and high temperatures than is that of Pease (56).

The parameters of equation 29 and the equilibrium relation were used to compute $k_3^r(T)$.

$$k_3^r(T) = k_3^f(T)/K_3(T) \tag{30}$$

2. Parameters for reaction 4: $H + Br_2 \rightleftarrows Br + HBr$

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[16] The use of the shock-wave technique as applied to the dissociation of bromine is discussed in Section III, C,3.

TABLE 10

Comparison of calculated with preliminary high-temperatures values for k_3^f

T	Experimental	Calculated[*]	Calculated[†]
°*K.*			
1396	8.9×10^{-9} 1.0×10^{-8}	2.0×10^{-8}	1.2×10^{-8}
1441	9.1×10^{-9} 7.9×10^{-9}	2.4×10^{-8}	1.5×10^{-8}

For the discussion of the experimental data see Section III,D,1.

[*] Values were calculated from the empirical equation given by Pease (56):

$$k_3^f = 4.56 \times 10^9 \sqrt{T} \exp[-18{,}780/RT]$$

[†] Values were calculated from the parameters given by equation 29.

Bodenstein and Jung (11) found that over the range 303–575°K.

$$k_4^f \simeq 8.4 k_3^r \qquad (31)$$

A recent shock-wave study of the hydrogen–bromine reaction (14) suggested that at about 1400°K. $5 < k_4^f/k_3^r < 15$. Equation 31 was used to compute $k_4^f(T)$. The equilibrium relation gave:

$$k_4^r(T) = k_4^f(T)/K_4(T) \qquad (32)$$

3. *Parameters for atom recombination reactions*

a. Interpretation of recombination as a three-body process

All investigators agree that the formation of a molecule from two atoms generally requires the presence of a third body to remove the excess energy. Two aspects of such a process suggest that the rate should show a decrease rather than an increase with temperature. First, the mutual approach of free atoms should be subject to a low energy barrier; second, any three-body interaction must occur as a sequence of two collisions, such as

(1) $Br + X \rightarrow BrX$
(2) $BrX + Br \rightarrow Br_2 + X'$

As the temperature increases, there will be a decrease in the time available for the approach of a second atom to a Br and an X which are close together as a result of the previous collision.

Clearly, the time which Br and X will spend in the vicinity of each other in the first collision will depend on the nature of X. Moreover, the possibility of X accepting energy to leave as the excited species X′ will vary with X. For example, recent flash-photolysis studies (19) have shown that I_2 is an order of magnitude more effective at room temperature than other third bodies for the recombination of iodine atoms. These studies, covering a wider range of $[I_2]/[X]$ and using an improved apparatus, showed that: (*a*) for the lowest values of $[I_2]/[X]$, there was an anomalous dependence of the rate constant[17] upon $[I_2]/[X]$;

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[17] The rate constant was a value obtained by extrapolating to time $t = 0$ in order to eliminate the presence of a thermal effect discussed in Section III,D,3,b.

(*b*) for larger values, the extrapolated constant was approximately a linear function of $[I_2]/[X]$. The linear dependence could be interpreted by supposing that both I_2 and X were acting as third bodies:

$$\begin{aligned}\frac{d[I]}{dt} &= k_{I_2}[I]^2[I_2] + k_X[I]^2[X] \\ &= \left[k_{I_2}\frac{[I_2]}{[X]} + k_X\right][I]^2[X]\end{aligned} \tag{33}$$

In the case of argon at room temperature this gave $k_{I_2}/k_A \simeq 250$. Other workers (15) have reported a ratio of 590 at room temperature and have stated that the ratio decreases with increasing temperature until at 1300°K. it is less than 30.

The experimental confirmation of the expected increase in rate with increasing temperature is reviewed in Section III,D,3,c,(6).

b. New experimental techniques: flash photolysis and shock waves

For the present our hope for satisfactory rate data for recombination reactions is based on two recently developed methods. The first, flash photolysis, uses an intense light of extremely short duration[18] to dissociate the molecules, and then follows the rate of atom recombination spectroscopically. Early flash-photolysis experiments gave irreproducible recombination rates. Part of these differences may be due to a previously ignored thermal effect (19). The importance of this effect was suggested by the restudy of the recombination of iodine atoms with an improved apparatus which disclosed a decrease with time of the three-body recombination constant. This decrease was attributed to heat released as a result of recombination which caused the temperature to rise while the heat loss to the surroundings cooled that part of the reaction cell near the walls. To maintain pressure equilibrium, the density of the warmer gases in the center decreased as the cooler gases near the wall contracted. Since the light beam traverses more of the central volume, the concentration of the halogen molecule in the light path is decreased. The rate was measured by the change in molecular absorption; hence this produced a decrease in the apparent recombination rate. Therefore the true rate constant was estimated by extrapolating the apparent constant to zero time.

Unfortunately, this thermal effect cannot be the complete source of these differences. A recent study (75) has reported unexplained erratic results from flash photolysis. For example, after experiments had given consistent values for about a year, experiments during the second year gave consistently higher values for the rate of iodine recombination even when the same operator used the same filling of the same cell. For data taken concurrently on bromine in argon, the high values were about 50 per cent larger than the low values.

The second technique of shock waves is well adapted to high-temperature measurements in contrast to the flash-photolysis method, which has thus far

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[18] In one recent study (75) the maximum light intensity was reached in 30 microsec., and the half-life was about 30 microsec.

only been used below about 550°K. A shock wave heats the gases rapidly to very high temperatures, and the molecular decomposition rate is followed spectroscopically. To interpret shock data, the temperature, density, and flow velocity of the gas are calculated (as functions of the experimentally measured shock velocity and of the assumed equation of state for the gas) from the Navier–Stokes equations (55). Thus far the method has given considerable scatter in computed rate constants (*cf.* Section III,D,3,c,(6)).

c. Experimental studies of reaction 1: $X + Br_2 \rightleftarrows 2Br + X$

As noted in the preceding section, flash-photolysis studies have given inexplicably erratic results, and shock waves have given constants with considerable experimental scatter. Therefore, earlier as well as more recent studies are listed in this section, together with some criticisms which have been made and some discussion of the results.

(1) Photochemical studies of the hydrogen–bromine reaction

The early work of Jost and Jung was complicated by a wall reaction (39, 41).[19] Since the surface reactions were suppressed in later studies by using higher pressures (34, 61),[20] and since Jost and Jung had to make arbitrary assumptions to account for the surface reactions,[21] their results have not been used.

Hilferding and Steiner (34) studied the photochemical reaction at about 200°C. After a careful analysis, they estimated that their data should be accurate to within about 55 to 65 per cent (34, p. 431). Rabinowitch (58) criticized their work and defended his own different values as follows: (*a*) their values depend upon the kinetic model and constants for the hydrogen–bromine reaction; (*b*) at the high bromine pressures used by Hilferding and Steiner, their assumption of uniform radiation throughout the containing vessel was far from justified; (*c*) their estimates of rate constants for different third bodies were based on an unjustified initial approximation. (At first Hilferding and Steiner assumed that the rate constants were the same for all third bodies. This is far from true.)

(2) Photochemical dissociation of bromine

The dissociation of bromine was studied by measuring the decrease in the molecular absorption coefficient of bromine in the illuminated vapor. In the photostationary state, the velocity of dissociation equals the rate of absorption of light quanta. If the heterogeneous recombination contributes insignificantly, then the equation for k_1^r is obtained by (*a*) equating the dissociation and three-body recombination rates and (*b*) using the experimental value for the stationary state [Br].

$$k_1^r = \frac{2N_{h\nu}}{[\mathrm{Br}]^2[\mathrm{X}]} \tag{34}$$

$N_{h\nu}$ = rate of absorption of light quanta.

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[19] For a review of this work, see Kassel (44).

[20] See Hilferding and Steiner (34, p. 399) and Rabinowitch and Wood (61, p. 910).

[21] See Kassel (44, p. 243).

The first experiments (59) were plagued by the same thermal effect found in flash-photolysis experiments (*cf.* Section III,D,3,b). This thermal effect was reduced in later experiments by using lower concentrations of halogen molecules (60, 61).

Rabinowitch defended these studies against Hilferding and Steiner's criticism of his neglect of convection by attempting to show that it was negligible under the experimental conditions (58). Although Rabinowitch and Wood believed that they had more accurate data for the recombination of iodine atoms than for bromine atoms, even their data for iodine agree only in order of magnitude with values obtained by flash photolysis. For $k_1^r \times 10^{15}$ cm.^{6} mole^{-2} sec.$^{-1}$, (helium:6.4; argon:13.8) compare with (helium:2.44 (19); argon:6.68 (19), 8.4 (52), 7.3 (63)). They estimated their accuracy as 10 per cent and 25 per cent for helium and argon as third bodies, respectively (61, p. 912).

One possible explanation for their larger values might be their neglect of I_2 as a third body. Flash-photolysis experiments described in Section III,D,3,a have shown that at room temperature iodine is more effective than argon by a factor of the order of 300 to 600.

In the studies with bromine Rabinowitch and Wood occasionally obtained values about 20 to 40 per cent smaller than those recorded in table 16. However, after each anomalous run, they were able to obtain again values comparable to those recorded. They suggested that water vapor may have caused the difficulty.

These results appear to have been accepted as the most reliable before the recent studies using flash photolysis and shock waves.

(3) Pressure changes accompanying dissociation and recombination

Shida (69) produced bromine atoms by irradiating mixtures of bromine with nitrogen and oxygen by a low-pressure mercury lamp and then studied the pressure changes which accompany the dissociation and recombination of bromine atoms. Unfortunately, the decrease in number of particles and increase in temperature produced by the liberation of energy upon forming bromine molecules were not the only sources of pressure change during the recombination process. A maximum and a minimum in the pressure curves were presumably caused by adsorption. The desorption was of the first order, and the substance adsorbed had a mean life of about 7 sec. Shida inferred that the bromine atom was adsorbed and that the rate-determining step was the evaporation of bromine atoms. Since the wall reaction was of the same order of magnitude as the homogeneous reaction, the values for the homogeneous rates which are recorded in table 16 are subject to considerable uncertainty.

(4) Flash-photolysis studies

Recent flash-photolysis studies[22] pose the following dilemma: (*a*) the precision within a sequence of runs may be good—in general, better than 10 per cent; (*b*) results from different sequences of runs using the same equipment and method differ by as much as 50 per cent; (*c*) values obtained by different investigators are subject to even greater discrepancies. The first thought that a competitive wall

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[22] See Sections III,D,3,a and b for further discussion.

reaction might produce these erratic results must answer the argument that the values for $[Br_2]/[X]$ used in flash-photolysis experiments were in the range that gave the pressure dependence corresponding to homogeneous recombination in the earlier photostationary studies of the dissociation of bromine.[23]

The authors hoped that, although their measurements varied erratically over long periods of time, data taken when the apparatus was giving consistently either high or low values would all be subject to about the same relative error and would therefore give a more reliable estimate for the temperature coefficient of the rate constant. Plots of log k versus T^{-1} from room temperature to about 160°C. gave activation energies of -2.0 and -1.2 kcal. mole^{-1} for argon and oxygen, respectively, as third bodies. This confirms the expected slow decrease of rate constant with increasing temperature.

Despite the erratic results which have been obtained thus far, flash photolysis seems to offer one of the best methods for studying reactions involving the recombination of atoms. Therefore, it is desirable to list possible errors suggested in a report on the recombination of bromine and iodine atoms (75).

(*a*) *Nonuniform illumination by the flash:* The possibility that the flash could have been more intense at the center than at the ends of the cell was checked both by masking the end of the cell and by using a cell only half as long. This was reported to have no effect upon the calculated rate.

(*b*) *Effect of excited states:* For studies at elevated temperatures, different rates of different excited states could be important. This could be simply tested in the case of iodine atoms, since molecules of iodine are dissociated by light from the continuum region ($<$ 4995 A.) into one excited $^2P_{\frac{1}{2}}$ and one normal $^2P_{\frac{3}{2}}$ atom, whereas light of the longer wavelengths in the banded region yields only normal atoms produced by predissociation. The discovery that the rate of recombination was the same for a frequency distribution centered above, as for one centered below 5000 A., suggested that excited atoms either fluoresce before combination or recombine at the same rate.

(*c*) *Relative effectiveness of bromine and of argon as third bodies:* If bromine, like iodine, were on the order of a few hundred times more effective than argon,[24] then most of the recombination in argon would actually have been effected by bromine molecules. The authors argued that this was unlikely because a 37 per cent variation in the $[Br_2]/[A]$ ratio gave only a 6 per cent variation in the rate constant for recombination computed under the assumption that only argon was effective. However, the erratic variation occurring between sequences of runs reduces the force of the argument. It is still possible that bromine may be significantly more effective.

(*d*) *Thermal effect:* Upon the basis of approximate calculations using a step-function model for the temperature gradient, the authors argued that the thermal effect (discussed in Section III,D,3,b) was negligible in their experiments. They argued that the linearity of their plots of $[Br]^{-1}$ vs. time excluded a significant thermal effect which would have decreased the rate of recombination with increasing time. The Cambridge restudy of the recombination of iodine atoms (19) sug-

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[23] See Rabinowitch and Wood (61, pp. 907–13).

[24] See Section III,D,3,a.

gested that the approximate linearity of their earlier plots of $[I]^{-1}$ vs. time was a result of less accurate data over a narrow range of variables and a partial cancellation of two opposing factors: (*a*) an increase in rate as recombination proceeds owing to the increasing concentration of the more effective third body, I_2; (*b*) a decrease in apparent rate due to the thermal effect. The authors of the study with bromine claimed that such a cancellation could not have occurred in their experiments, since the $[Br_2]$ varied only from 95 to 99 per cent of its initial value. They attributed the greater thermal effect in the experiments with iodine to the use of measurement times much longer than the time of 1 millisec. used in the experiments with bromine.

(5) Shock-wave studies

Palmer and Hornig (55) have measured the dissociation of bromine, both pure and diluted with argon, from 1200°K. to 2225°K. They compressed bromine (or mixtures of bromine and argon) at pressures of 1 to 4 cm. of mercury by shock waves produced by helium at pressures up to 12 atm. In addition, Britton and Davidson (14a) have studied mixtures of bromine and argon from 1400° to 2700°K. The change in bromine concentration was followed by measuring the absorption of bromine. Palmer and Hornig determined the extinction coefficient as a function of temperature from the absorption just after the shock before appreciable dissociation occurred. A wavelength (4390 A.) was selected in the pure continuum region in order to reduce the deviations from Beer's law occurring in banded regions.

The authors reported that the most obvious limitation upon the precision of their rate constants was the estimation of an angle in the oscilloscope trace which measured the initial rate of change of absorption of bromine. The original article should be consulted for discussion of errors.

The rather widely scattered experimental rates could be correlated by either of two distinct theoretical models: (*1*) a simple bimolecular collision in which the energy of relative motion along the line of centers must exceed the activation energy (*cf.* equation 14); (*2*) a bimolecular collision in which some rotations and vibrations of the colliding molecules participate (*cf.* equation 15).

Empirical fitting of experimental rates gave the equations for rate constants in the units of cubic centimeters per mole per second:

$$\frac{d[Br_2]}{dt} = k_A[Br_2][A] + k_{Br_2}[Br_2]^2 \qquad (35)$$

Model 1:

$$\text{a.}\quad k_A = 2.52 \times 10^{11} T^{\frac{1}{2}} \exp(-3.069 \times 10^4/RT) \qquad (36a)$$

$$\text{b.}\quad k_{Br_2} = 2.70 \times 10^{11} T^{\frac{1}{2}} \exp(-2.921 \times 10^4/RT) \qquad (36b)$$

Model 2:

a. Using only shock-wave data:

$$k_A = 1.99 \times 10^8 T^{\frac{1}{2}} (E_0/RT)^{4.46} \exp(-E_0/RT) \qquad (37a)$$

Combining shock-wave data with flash-photolysis data at 298° and 430°K. (75):

$$k_{\mathrm{A}} = 1.39 \times 10^{11} T^{\frac{1}{2}} (E_0/RT)^{1.97} \exp(-E_0/RT) \tag{37b}$$

b. $$k_{\mathrm{Br}_2} = 5.98 \times 10^{6} T^{\frac{1}{2}} (E_0/RT)^{5.94} \exp(-E_0/RT) \tag{38a}$$

or

$$k_{\mathrm{Br}_2} = 2.40 \times 10^{10} T^{\frac{1}{2}} (E_0/RT)^{3.0} \exp(-E_0/RT) \tag{38b}$$ [25]

Although model 1 gave a reasonable estimate for the collision efficiency (of the order of 5 per cent for a collision diameter of about 3 A.), it gave an apparent activation energy about 15 kcal. less than the energy of dissociation. Palmer and Hornig argued that if a molecular complex were formed, it might stabilize one of the bromine atoms in the collision. This could reduce the energy of activation perhaps 0.5 kcal. for argon and 3 kcal. for bromine as a third body, but certainly not 15 kcal. Therefore, the empirical equations for model 1 seem physically unreasonable.

A bromine molecule colliding with an argon atom might contribute energy from one rotational and one vibrational degree of freedom; if a bromine molecule replaced the argon atom, it might supply energy from one additional vibrational and two rotational degrees of freedom. This would give maximum exponents of (E_0/RT) of 1.5 for argon and 3.5 for bromine. However, if all energy of relative translational motion contributed, rather than just the energy along the line of centers, this would lead to an added term of (E_0/RT). The latter maximum exponents are greater than those for equations 37b and 38b but less than those for equations 37a and 38a. Palmer and Hornig concluded that equations 37b and 38b were more satisfactory.

(6) Summary of results: suggested values for the parameters

The recombination rate constant for bromine atoms still seems uncertain to a factor of 2 or more. Temperature coefficients have been measured only for the following three third bodies: oxygen and argon (by flash photolysis between 300° and 430°K. (75); bromine and argon (by shock waves between 1200° and 2200°K. (55)).

Flash-photolysis experiments are still subject to unexplained erratic variation (see Section III,D,3,b), and the shock-wave studies give considerable scatter. In fact, the scatter was so great that Britton and Davidson (14a) found that their shock-wave values alone were not sufficient to determine the sign of the recombination rate which varies only slowly with temperature. The uncertainty in the temperature coefficient is illustrated by the difference between equation 37a for the rate of dissociation of bromine (based only on shock-wave data) and equation 37b (based on both shock-wave and low-temperature flash-photolysis data).

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[25] Equation 38a, which was derived by empirically fitting the rate data, was considered unsatisfactory because of the low collision efficiency and because of the unreasonably large exponent of (E_0/RT). Equation 38b was proposed as a more reasonable one which would still correlate the wide scatter of the data rather well.

The workers with flash photolysis suggested that bromine was not a vastly more effective third body than argon even at room temperature (see Section III, D,3,c,(4)). However, this possibility cannot be definitely excluded. If bromine were as effective, compared with argon, as iodine compared with argon, then the true constant for argon as a third body would be several-fold smaller than the present ones obtained by flash photolysis.

The rate of dissociation (which shock data measure) varies rapidly with temperature, while the rate of recombination varies only slowly. Therefore, the best procedure for obtaining empirical equations consists in (*a*) computing an experimental recombination rate from the measured dissociation rate and the corresponding equilibrium constant by equation 16, (*b*) fitting the experimental recombination rates to an empirical function, and (*c*) obtaining the function for the dissociation rate by dividing the empirical function for recombination by the equilibrium constant. Obviously, this process cannot reduce the basic uncertainty in the data. The maximum estimated error of 50° at high temperatures and 30° at low temperatures (55) leads to possible errors in the correlation of dissociation rates with temperature of a factor of 20 per cent or 30 per cent, respectively. Thus, Britton and Davidson (14a) found that the scatter of their recombination rates was so great that they were unable to determine even the sign of the temperature dependence. When the data of Palmer and Hornig (55) on the dissociation rate were recomputed following the foregoing scheme, the rates showed a definite trend with temperature which could be correlated by the parameter values (*cf.* table 11):

$$\mathrm{X} = \text{argon}: g_1^r = 1.19 \times 10^{+26};\ h_1^r = -3.5 \pm 0.5;\ \Delta E_1^r = 0 \qquad (39)$$

TABLE 11

Shock-wave values for k_1^r, X = argon

T	$k_1^r \times 10^{-14}$	$k_1^r T^{3.5} \times 10^{-25}$	Per Cent Deviation
°*K.*			
1310	21.8	17.74*	+50*
1330	14.24	12.22	+3
1380	27.8	27.14*	+129*
1425	5.54	6.05*	−49*
1520	7.82	10.71	−10
1580	6.16	9.66	−18
1750	5.30	11.88	+0.2
1840	2.12	5.67*	−52*
1840	12.04	32.18*	+172*
1965	4.16	13.99	+18
2050	3.16	12.32	+4
2080	2.70	11.08	−7
2225	2.50	13.00	+10
Average		11.86	8.8

The experimental values were computed as described in the discussion preceding equation 39. The rate law is

$$\frac{\mathrm{d[Br]}}{\mathrm{d}t} = -k_1^r[\mathrm{Br}]^2[\mathrm{A}]$$

and the units of k_1^r are mole² cm.⁻⁶ sec.⁻¹ The starred values were excluded in computing the two averages. Column 4 is the per cent deviation of column 3 from its average value.

TABLE 12

Flash-photolysis values for k_1^r, X = *argon*

T	$k_1^r \times 10^{-15}$	$(k_1^r T^{2.75}) \times 10^{-22}$	Per Cent Deviation	$[k_1^r T^{3.5} \exp(+\Delta E/RT)] \times 10^{-24}$	Per Cent Deviation
°*K.*					
298	7.46	4.75	+0.85	8.37	+1.45
299	7.30	4.69	−0.42	8.26	+0.12
300	7.44	4.83	+2.54	8.50	+3.03
302	7.24	4.78	+1.49	8.41	+1.94
333	5.44	4.70	−0.21	8.19	−0.73
347	4.50	4.36	−7.43	7.58	−8.12
348	4.94	4.82	+2.33	8.39	+1.70
364	4.44	4.90	+4.03	8.53	+3.39
372	3.96	4.64	−1.49	8.08	−2.06
380	3.58	4.45	−5.52	7.75	−6.06
394	3.44	4.72	+0.21	8.24	−0.12
405	3.10	4.59	−2.55	8.03	−2.67
429	2.74	4.75	+0.85	8.37	+1.45
433	2.80	4.98	+5.73	8.78	+6.42
Average		4.71	2.55	8.25	2.80

The experimental values were obtained from reference 75. The rate law is

$$\frac{d[\mathrm{Br}]}{dt} = -\,k_1^r[\mathrm{Br}]^2[\mathrm{A}]$$

and the units of k_1^r are mole^2 cm.$^{-6}$ sec.$^{-1}$ Columns 4 and 6 are the per cent deviations of columns 3 and 5 from their average values. The calculated values in columns 3 and 5 use the parameters of equations 40a, b.

The limiting values (k_1^r = 3.0, 4.0) gave opposite trends with temperature of borderline significance. The more consistent flash-photolysis experiments gave the following values (*cf.* table 12):

$$\mathrm{X} = \mathrm{argon}\colon g_1^r = 4.71 \times 10^{+22};\ h_1^r = -\,2.75 \pm 0.05;\ \Delta E_1^r = 0 \qquad (40a)$$

or

$$g_1^r = 8.25 \times 10^{+24};\ h_1^r = -\,3.5 \pm 0.05;\ \Delta E_1^r = 267.85\ R \qquad (40b)$$

Unfortunately the two sets of data cannot be correlated by a single equation of the form of equation 11. Comparison of the two indicates an overall temperature dependence of the order of $T^{-1.5}$. A similar discrepancy between results from the two methods occurs also in the case of the recombination of iodine atoms. In the latter case, the high-temperature shock-wave rates varied far more rapidly [$\exp(+4560/RT)$] than low-temperature flash-photolysis rates [$\exp(+1400/RT)$] (15). Nevertheless, the temperature dependence of the flash-photolysis rates agrees well with the overall trend, $\exp(+1330/RT)$, predicted by comparing the rate at room temperature with a rate in the middle of the range of shock-wave temperatures where the measurements were believed to be somewhat more reliable.

Since shock-wave rates have been shown above to be subject to uncertainty which can alter the order of their temperature variation, the data on the recombination of bromine atoms have been correlated by a procedure suggested by the studies of the recombination of iodine atoms. The value at 1750°K., which lay

TABLE 13

A. Correlation of shock-wave and flash-photolysis data for X = *argon*

T	$k_1^r \times 10^{-15}$	$[(k_1^r\ T^{-0.1} \exp +\Delta E/RT)] \times 10^{-14}$	Per Cent Deviation
°K.			
298	7.46	1.41	−1.40
299	7.30	1.39	−2.80
300	7.44	1.44	+0.70
302	7.24	1.43	0.00
333	5.44	1.45	+1.40
347	4.50	1.35	−5.59
348	4.94	1.50	+4.90
364	4.44	1.52	+6.29
372	3.96	1.44	+0.70
380	3.58	1.37	−4.20
394	3.44	1.45	+1.40
405	3.10	1.39	−2.80
429	2.74	1.41	−1.40
433	2.80	1.47	+2.80
Average		1.43	2.60

The calculated values were computed as described in this section preceding equation 41. The rate law is

$$\frac{d[\mathrm{Br}]}{dt} = -k_1^r[\mathrm{Br}]^2[\mathrm{A}]$$

and the units of k_1^r are mole^2 cm.$^{-6}$ sec.$^{-1}$ Column 4 is the per cent deviation of column 3 from its average value.

B. Correlation of shock-wave and flash-photolysis data for X = *argon*

T	k_1^r exptl. $\times 10^{-14}$	k_1^r calcd. $\times 10^{-14}$	T	k_1^r exptl. $\times 10^{-14}$	k_1^r calcd. $\times 10^{-14}$
°K.			°K.		
1310	21.8	6.35	1840	2.12	5.26
1330	14.24	6.29	1840	12.04	5.26
1380	27.80	6.14	1965	4.16	5.11
1425	5.54	6.02	2050	3.16	5.03
1520	7.82	5.80	2080	2.70	5.00
1580	6.16	5.67	2225	2.50	4.87
1750	5.30	5.38	—		

The experimental values were computed as described in the paragraph preceding equation 39. The rate law is

$$\frac{d[\mathrm{Br}]}{dt} = -k_1^r[\mathrm{Br}]^2[\mathrm{A}]$$

and the units of k_1^r are mole^2 cm.$^{-6}$ sec.$^{-1}$ The calculated values were computed from the parameters of equation 41. As discussed above, these parameters were obtained by fitting the flash-photolysis data with the 1750° datum in the *shock-wave experiments.*

in the mid-range of measurements and near the smoothed curve for shock-wave values (55), was combined with low-temperature flash-photolysis values. The combined data did not fit an inverse T^{-n} dependence but could be fitted by the following parameters (*cf.* table 13):

$$\mathrm{X} = \text{argon}: g_1^r = 1.43 \times 10^{+14};\ h_1^r = 0.1;\ \Delta E_1^r = -1013.0 \qquad (41)$$

The only low-temperature measurement for X = bromine was seen in Section III,D,3,c,(1) to be only of qualitative significance. Table 14 on shock-wave measurements shows such a great scatter that the empirical equation

TABLE 14

Shock-wave values for k_1^r, X = bromine

T	$k_1^r \times 10^{-15}$	$k_1^r T^4 \times 10^{-27}$	Per Cent Deviation
°K.			
1010	69.20	71.97*	
1050	36.46	44.34*	
1100	11.78	17.25*	
1220	4.01	8.89	−9.1
1240	6.28	14.88	+52.2
1245	2.89	6.94	−29.0
1320	3.24	9.84	+0.6
1370	3.48	12.26	+25.4
1390	4.12	15.38	+57.3
1425	1.97	8.12	−17.0
1445	1.44	6.28	−35.8
1550	1.11	6.41	−34.5
1610	1.31	8.80	−10.0
Average		9.78	27.1

The rate law is

$$\frac{d[\mathrm{Br}]}{dt} = -k_1^r[\mathrm{Br}]^2[\mathrm{Br}_2]$$

and the units of k_1^r are mole² cm.⁻⁶ sec.⁻¹ The starred values were believed to be less accurate for experimental reasons and were excluded from the averages of column 3.

$$\mathrm{X} = \mathrm{Br}_2\colon g_1^r = 9.78 \times 10^{+27};\ h_1^r = -4.0;\ \Delta E_1^r = 0 \tag{42}$$

can do little more than suggest that (a) bromine appears to be more effective as a third body by about a factor of 2 over the temperature range common to the two measurements, and (b) the rate may decrease somewhat more rapidly with increasing T for X = bromine than for X = argon. The discussion of the representation for X = argon suggests that equation 42 probably does not represent even the true high-temperature variation of k_1^r.

In lieu of accurate data the rate of recombination for X = bromine has been taken to be just twice that for X = argon. Actually, the two rates should have a different temperature dependence. For X = oxygen, the values suggested by flash-photolysis studies have been adopted (75). In each case the value of the dissociation rate was computed from the equation:

$$k_1^f(T) = K_1(T)k_1^r(T) \tag{43}$$

As an aid in estimating values for other third bodies, various results have been collected in table 16.

Extensive flame calculations were begun before recent flash-photolysis and shock-wave studies were made. Since at that time no temperature coefficients had been determined, the following simple but unrealistic equations were used:

$$k_1^r = 1 \times 10^{+16} \text{ for all X, } T \tag{44}$$

$$k_1^f = K_1(T)k_1^r$$

TABLE 15

Parameters for reaction 1: $Br_2 + X \rightleftarrows 2Br + X$

X	g_1^r	h_1^r	ΔE_1^r	g_1^f	h_1^f	ΔE_1^f
O_2	$2.08 \times 10^{+14}$	0.00	$-623.7\ R$	$+2.9938\ 44512 \times 10^{+16}$	-0.50	$+4.4813\ 19710 \times 10^{+4}$
Br_2	$2.86 \times 10^{+14}$	$+0.10$	$-1013.0\ R$	$+4.1165\ 36204 \times 10^{+16}$	-0.40	$+4.4039\ 58403 \times 10^{+4}$
A	$1.43 \times 10^{+14}$	$+0.10$	$-1013.0\ R$	$+2.0582\ 68102 \times 10^{+16}$	-0.40	$+4.4039\ 58403 \times 10^{+4}$

The parameters apply to the rate equation:

$$\frac{d[Br]}{dt} = k_1^f[Br_2][X] - k_1^r\,[Br]^2\,[X]$$

The units of k_1^r are mole^2 cm.$^{-6}$ sec.$^{-1}$ The parameters for the forward reaction were computed from equation 43 using the parameters of table 5 for $K_1(T)$.

TABLE 16

Experimental values for the rate of recombination of bromine atoms

Source of Data	Temperature	X									
		He	A	CH_4	CO_2	H_2	N_2	O_2	Br_2	HBr	HCl
	°K.										
(34)	490	0.94	0.22			2.50	1.64		5.2	4.2	9.4
(41, 41a)	499					11.4					
(61)	≃293	2.8	4.7	13.1	19.6	8.0	9.1	11.6			
(69)							3.9	10.0			
(75)	293		6.1				6.8	16			

The values are for $k_1^r \times 10^{-15}$ cm.^{6} mole^{-2} sec.$^{-1}$, the three-body recombination rate in the equation

$$d[Br]/dt = -\,k_1^r\,[Br]^2[X]$$

Note that there are small discrepancies between the values reported by Rabinowitch in his different articles. The flash-photolysis value for argon (75) is an average of a set of sequences of runs. The values within each sequence had average deviations of 10 per cent or less, but the different sequences had average values ranging from 5.92 to 7.46 × 10^{+15}.

d. Experimental studies of reaction 2: $H_2 + X \rightleftarrows 2H + X$

Despite numerous studies there is no agreement on the relative importance of H_2 and of H as third bodies for homogeneous recombination, of wall reactions under the various experimental conditions, and of processes such as diffusion in flow systems. Kassel (43) has summarized excellently the earliest work (9, 31, 65, 66, 67, 70, 73) which later studies have superseded. These more recent studies are grouped according to method and discussed critically in the following subsections (1 to 5).

(1) Determination of H by the rate of conversion of para-hydrogen to ortho-hydrogen

Farkas and Sachsse (22) irradiated a mixture of hydrogen and mercury in a 100-ml. quartz vessel with a mercury resonance lamp and produced a low stationary-state concentration, $[H] \simeq 0.001$ mm. Hg. As evidence that the reaction was homogeneous in quartz vessels at sufficiently high light intensities and pressure of hydrogen, they observed that (*a*) the [H] varied as $\sqrt{[H_2]}$ (*vide infra*), and (*b*) the rate was not affected by changing the size of the vessel. However, heterogeneous reaction must have occurred, since the reaction was catalyzed by dust, grease, and other impurities. Since the wall reaction was assumed to be negligible, the steady-state rate of homogeneous recombination was equated to the rate of production, which was given by twice the rate of absorption of quanta from the excited mercury atom:

$$2I = k_1^r[\mathrm{H}]^2[\mathrm{H_2}] \tag{45}$$

where I = rate of absorption of quanta.

The [H] was computed as follows: Since ortho- and para-hydrogen have different thermal conductivities, the rate of conversion of para-hydrogen to orthohydrogen was followed by measuring the change in thermal conductivity of a nonequilibrium mixture. Previous work on this conversion (21)[26] had shown that over a temperature range of 600–750°C. in static experiments:

$$(P_t - P_\infty) = (P_0 - P_\infty)\exp(-k_2 t\sqrt{[\mathrm{H_2}]}) \tag{46}$$

where

P_t = the pressure of para-hydrogen at time t
$P_\infty = \lim\limits_{t\to\infty} P_t$
$P_0 = P_t$ at $t = 0$
$k_2 = 1.02 \times 10^{12}\exp[-58{,}700/RT]$ (in the units of $(\sqrt{\mathrm{l./mole}})$ sec.$^{-1}$)

This rate law was interpreted by the mechanism:

$$\mathrm{H_2} \rightleftarrows 2\mathrm{H}\ \text{(equilibrium)} \tag{47}$$

$$\mathrm{H} + \text{para-H}_2 \rightleftarrows \text{ortho-H}_2 + \mathrm{H}$$

If H is assumed to be in equilibrium with H_2, then equation 46 yields

$$[\mathrm{H}] = \frac{\sqrt{K_1}}{k_2 t}\ln\left(\frac{P_0 - P_\infty}{P_t - P_\infty}\right) \tag{48}$$

Two obvious limits on the accuracy of k_1^r are the accuracy in the measurement of the absorbed light and the uncertainty of k_2. As tables 10 and 17 show, extrapolation of a rate constant determined at a temperature of 600–750°C. to 24°C. could introduce an error of several-fold.

At 24°C. and a hydrogen pressure of 200 mm. of mercury, Farkas and Sachsse calculated:

$$k_2^r = 3.4 \times 10^{16}\ \mathrm{cm.^6 mole^{-2}\ sec.^{-1}} \tag{49}$$

$$\frac{\mathrm{d[H]}}{\mathrm{d}t} = -k_2^r[\mathrm{H}]^2[\mathrm{H_2}]$$

When newer, more accurate data are used for K_1, the value is

$$k_2^r = 2.2 \times 10^{16}\ \mathrm{cm.^6\ mole^{-2}\ sec.^{-1}} \tag{50}$$

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[26] See Kassel (43, pp. 136–7).

(2) Generation of hydrogen atoms by a Wood discharge tube; measurement of the pressure change

Smallwood (71) generated hydrogen atoms in a Wood discharge tube to obtain mixtures of from 20–30 mole per cent hydrogen atoms at total pressures of a few tenths of a millimeter of mercury. He followed the recombination in a static system by measuring the pressure change. He reported that a bimolecular wall reaction could be suppressed by flushing the apparatus with atomic hydrogen. His claim that the rate constant for atomic hydrogen was at least fifty times as large as that for molecular hydrogen revived the surprising suggestion of Senftleben and Riechemeier (66) that H was vastly more effective. The value at 298°K. was reported as

$$\frac{\mathrm{d}[\mathrm{H}]}{\mathrm{d}t} = -k_2^r[\mathrm{H}]^3 \tag{51}$$

$$k_2^r = (1.7 \pm 0.3) \times 10^{16}\ \mathrm{cm.}^6\ \mathrm{mole}^{-2}\ \mathrm{sec.}^{-1}$$

(3) Measurement of [H] by the Wrede slit technique

Steiner (72) made a new study to answer Amdur's criticism (1) of his earlier study (73). A Wood discharge tube gave as high as 80 per cent concentration of atoms at total pressures of several tenths of a millimeter of mercury. Steiner measures the [H] at the entrance to the recombination tube by the Wrede slit technique (84) and relative values along the tube spectroscopically. Although he tried to poison the walls of the tube by the constant addition of about 3 per cent water vapor, he did not eliminate the wall reaction, and therefore he was able to determine only an upper limit for the rate of homogeneous recombination. At 20°C. for H_2 as a third body he found that $k_2^r < 1.3 \times 10^{+16}$ and suggested that the more probable value was

$$k_2^r = 1.1 \times 10^{16}\ \mathrm{cm.}^6\ \mathrm{mole}^{-2}\ \mathrm{sec.}^{-1} \tag{52}$$

$$\frac{\mathrm{d}[\mathrm{H}]}{\mathrm{d}t} = -k_2^r[\mathrm{H}]^2[\mathrm{H}_2]$$

He decided that the recombination rate for H as a third body could be at most one-tenth that for H_2.

(4) Measurement of [H] in a flow system by heat transferred to a catalyst-calorimeter

By virtue of its completeness, Amdur's 1938 paper (3) supersedes earlier studies (2, 7, 8, 70) with this method. Amdur used essentially Smallwood's technique (70). Hydrogen at pressures of a few tenths of 1 mm. of mercury was dissociated to give mole-fractions of hydrogen atoms in the range 0.04 to 0.69. The [H] was determined by the heat of recombination absorbed by a platinum catalyst calorimeter inserted at various positions of a flow tube. Smallwood (70) had previously shown that the catalyst was almost completely efficient.

Objections to determining H in a flow system by a catalyst-calorimeter were raised by Smallwood in his later paper (71) and by Steiner (72). Smallwood discounted Amdur and Robinson's defense (7, pp. 1402–3) of the method and argued that the abrupt recombination at the catalyst gave a pressure drop that caused diffusion in the gas mixture.

Since Amdur surmised that the disagreement between the various investigations might be caused by the fact that rather inaccurate kinetic data covering a narrow range of experimental conditions could not define a unique mechanism, he decided to cover a wide range of experimental conditions. He employed seven different pumping speeds and varied the mole-fraction of H from 0.04 to 0.69. In analyzing his data, he first found an empirical equation to represent the total pressure and mole-fraction of H as a function of distance through the tube. Then he used these smoothed values of mole-fraction and pressure, together with their first and second derivatives with respect to distance, to solve for the rate constants in the equation

$$\frac{-\mathrm{d}[\mathrm{H}]}{\mathrm{d}t} = k_1[\mathrm{H}] + k_2[\mathrm{H}]^2 + k_3[\mathrm{H}]^2[\mathrm{H}_2] + k_4[\mathrm{H}]^3 \qquad (53)$$

where k_1, k_2 = wall-reaction constants, and k_3, k_4 = homogeneous reaction constants.

In order to see how well his smoothed data determined the mechanism, he then assumed that various of the processes were negligible (i.e., he equated the corresponding rates to zero) and computed the mole-fraction of H using the calculated values for the remaining rate constants. He eliminated, as less probable, those mechanisms that gave deviations two to three times larger than the better ones. However, deviations even on the best runs lay between 3 and 8 per cent. On this basis he decided that collisions with H_2 had to be included, but that alternative assumptions could be made about the wall reactions. One of the five possible mechanisms excluded H as an effective third body; the other four gave a larger rate constant for H than for H_2. Nevertheless, all the rate constants for homogeneous recombination[27] lay between 0.9 and 3.1×10^{16} mole^{-2} cm.^{6} sec.$^{-1}$ The temperature was 30°C.

Whereas Amdur found that it was necessary to use highly consistent data in the simultaneous solution for rate constants, his original data deviated by about 3 per cent from his smoothed curves. Furthermore, although diffusion could be treated only roughly and made only a small contribution to the equations for mole-fraction and pressure, neglect of diffusion gave an enormous variation in size and even negative values when the rate constants were determined simultaneously. The importance of diffusion suggests that Smallwood (71) may have been correct in his surmise that the effect of the catalyst-calorimeter cannot be ignored. Certainly the critical effect of diffusion casts doubt upon results which treat it only roughly. For this reason, and also because of the rather large deviations of even the best mechanisms, the exclusion of other kinetic models must remain in doubt.

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[27] This statement excludes the one mechanism in which the rate constant for H as a third body was equated to zero.

Amdur's work on alternative interpretations shows beautifully the danger lurking in the plausible explanation of inaccurate data.

(5) Measurement of [H] in a static system with large H_2 by pressure changes

Like Farkas and Sachsse (22), Shida (68) used collisions of the second type between excited mercury atoms and hydrogen molecules to produce low concentrations of hydrogen atoms at a high pressure of hydrogen molecules (650 mm.). Two processes produce pressure changes: the variation in [H] and the rise in temperature produced by the heat released upon recombination. An oscillograph recorded pressure measurements by an elec-capacity differential manometer. Because of the high H_2 pressure and low [H], Shida reduced the significance of wall reactions and of recombination with H as a third body. He obtained

$$k_2^r = 4.4 \times 10^{16} \text{ cm.}^6 \text{ mole}^{-2} \text{ sec.}^{-1} \qquad (54)$$

$$\frac{d[H]}{dt} = -k_2^r[H]^2[H_2]$$

(6) Summary of results; suggested values for the parameters

Farkas and Sachsse, Amdur, and Shida all obtained values greater than 10^{+16} at about room temperature for the recombination of hydrogen atoms with H_2 as the third body. Therefore, it has been assumed that

$$k_2^r(293°) = 2 \times 10^{+16}$$

$$\frac{d[H]}{dt} = -k_2^r[H]^2[H_2] \qquad (55)$$

Since no data on the temperature coefficient are available, it is necessary to use the value of equation 55 at one temperature and to choose a reasonable functional form for the temperature dependence. The discussion of the recombination of bromine atoms in Section III,D,3,c,(6) suggested that the following equation should be qualitatively but not quantitatively correct. It is recommended for use in lieu of actual data.

$$X = H_2\colon g_2^r = \mathit{1.0} \times 10^{+20};\ h_2^r = -\mathit{1.5};\ \Delta E_1^r = \mathit{0} \qquad (56)$$

Although there are no quantitative data on the relative effectiveness of various third bodies, Amdur's experiments (3) suggest that the efficiencies of H_2 and H are of the same magnitude, and the experiments of Senftleben and Hein (64) suggest that the efficiencies of the inert gases increase with increasing molecular weight.

Since the first flame studies were begun before measurements of the temperature coefficient of the recombination of bromine atoms were available as a basis for suggesting a qualitatively reasonable functional dependence upon temperature, the following unrealistic equation has been used in flame calculations:

$$k_2^r = 2 \times 10^{+16} \text{ for all } T \text{ and X}$$

$$\frac{d[H]}{dt} = -k_2^r[H]^2[X] \qquad (57)$$

The dissociation rate was obtained for both equations 55 and 57 from the equilibrium relation:

$$k_2^f(T) = K_2(T)k_2^r(T) \tag{58}$$

It is fortunate that at least in the case of the flame produced by burning an equimolar mixture of hydrogen and bromine (17), the contribution of reaction 2 to the differential equation appears to be of the order of 1/1000th that of reactions 3 and 4. Nevertheless, the dissociation of H_2 should become more important at higher temperatures, and it would be desirable to obtain significant information about the recombination process.

e. Reaction 5: $X + H + Br \rightleftarrows HBr + X$

There are no data on this reaction. For flame studies, this rate has been given an arbitrary equation based on the equations assigned for the recombination of hydrogen atoms and of bromine atoms. When equation 44 is used for the recombination of bromine atoms and equation 57 for the recombination of hydrogen atoms, the recombination rate has been given the value:

$$k_5^f = \mathit{1.5} \times 10^{16} \text{ for all } T, \text{X} \tag{59a}$$

When equation 56 is used for the recombination of hydrogen atoms, it has been given the parameters:

$$g_5^f = \mathit{1.5} \times 10^{+20};\ h_5^f = -\mathit{1.5};\ \Delta E_5^f = \mathit{0} \text{ for all X}$$

$$\frac{\mathrm{d[H]}}{\mathrm{d}t} = k_5^f[\mathrm{H}][\mathrm{Br}][\mathrm{X}] \tag{59b}$$

In both cases the dissociation rate was obtained from the equilibrium relation:

$$k_5^r(T) = k_5^f(T)/K_5 \tag{60}$$

4. Summary of suggested values

The bases for assigning these values and their uncertainties have been discussed in Section III,D,1-3. Table 10 shows how the scatter of even the best rate data on the hydrogen–bromine reactions has led to empirical equations that predict marked differences in the high-temperature reaction rates. Table 17 shows the effect of using data from different temperature ranges to determine an empirical rate equation in the case of the bimolecular hydrogen–iodine reaction.

Clearly, lengthy extrapolation of rate data introduces order of magnitude uncertainty. Nevertheless, since in calculations it is sometimes desirable to maintain thermodynamic consistency, the parameters in table 18 have been recorded to ten digits. The graphs of the data have been included for use when such consistency is not important.

IV. TRANSPORT PROPERTIES

The solution of the hydrogen–bromine flame equations requires a knowledge of the thermal conductivity and of the diffusion coefficients over a 1400°K. range. The terms involving viscosity have been omitted from the hydrodynamic equa-

TABLE 17

Extrapolated values for the specific rate constant for the hydrogen–iodine reaction

T	$k_\alpha(T)$	$k_\beta(T)$	$k_\gamma(T)$
°K.			
500	3.58×10^{-6}	1.76×10^{-6}	4.42×10^{-6}
1000	$1.81 \times 10^{+4}$	$2.98 \times 10^{+4}$	$1.21 \times 10^{+4}$
1500	$3.39 \times 10^{+7}$	$8.36 \times 10^{+7}$	$1.85 \times 10^{+7}$

The subscripts α, β, and γ identify the temperature range used to determine the parameters of the empirical rate constant by the criterion of best fit. The ranges are:

$$k_\alpha(T) = 2.05 \times 10^{10}\ T^{\frac{1}{2}} \exp[-43{,}714/RT],\ 556\text{–}781°\text{K}.$$
$$k_\beta(T) = 1.13 \times 10^{13}\ T^{\frac{1}{2}} \exp[-46{,}116/RT],\ 660\text{–}781°\text{K}.$$
$$k_\gamma(T) = 7.40 \times 10^{11}\ T^{\frac{1}{2}} \exp[-42{,}493/RT],\ 556\text{–}660°\text{K}.$$

Cf. Kassel (43, p. 150).

TABLE 18

Numerical parameters for the specific rate constants of the reactions

	g_i	h_i	ΔE_i
k_1^f	$+4.1165\ 36204 \times 10^{+16}$	-0.40	$+4.4039\ 58403 \times 10^{+4}$
k_2^f	$+6.5375\ 17476 \times 10^{+18}$	-1.00	$+1.0299\ 14225 \times 10^{+5}$
k_3^f	$+3.4600\ 00000 \times 10^{+10}$	$+1.00$	$+1.6640\ 00000 \times 10^{+4}$
k_4^f	$+6.4233\ 81061 \times 10^{+12}$	$+0.50$	$+1.1096\ 92500 \times 10^{+3}$
k_5^f	$+1.5000\ 00000 \times 10^{+20}$	-1.50	0
k_1^r	$+2.8600\ 00000 \times 10^{+14}$	$+0.10$	$-2.0130\ 23470 \times 10^{+3}$
k_2^r	$+1.0000\ 00000 \times 10^{+20}$	-1.50	0
k_3^r	$+7.6468\ 82215 \times 10^{+11}$	$+0.50$	$+1.1096\ 92500 \times 10^{+3}$
k_4^r	$+6.4479\ 09683 \times 10^{+10}$	$+1.00$	$+4.2518\ 20000 \times 10^{+4}$
k_5^r	$+2.1672\ 67028 \times 10^{+20}$	-1.50	$+8.7461\ 11500 \times 10^{+4}$

$$k_i^f = g_i^f T^{h_i^f} \exp(-\Delta E_i^f/RT)$$

$$k_i^r = g_i^r T^{h_i^r} \exp(-\Delta E_i^r/RT)$$

The concentrations are expressed in the units of mole cc.$^{-1}$ These values are based on the equilibrium constant formulae using the rounded average heat capacities (*cf.* table 5). For reaction (^r_i), the third body X is assumed to be Br_2.

tions. For flames with a burning velocity less than one-tenth the speed of sound the equation of motion involving viscosity can be neglected (38, p. 780). Since the pressure is relatively low and is practically constant, the V-T relation can be obtained from the ideal gas law (37). Furthermore, terms involving kinetic energy can be neglected in the energy balance equation. Present flame studies include only first-order terms and neglect second-order transport effects such as thermal diffusion.

Although the hydrogen–bromine system is the best-known multicomponent flame system, much of the required information is not in the literature. The estimation and extrapolation of necessary parameters can be accomplished using either empirical equations or the results of the rigorous kinetic theory of dilute gases which gives the transport coefficients as functions of the intermolecular potential.

The techniques for direct experimental determination of thermal conductivity and diffusion coefficients will be discussed in Section IV,A and the methods of estimation in Section IV,B.

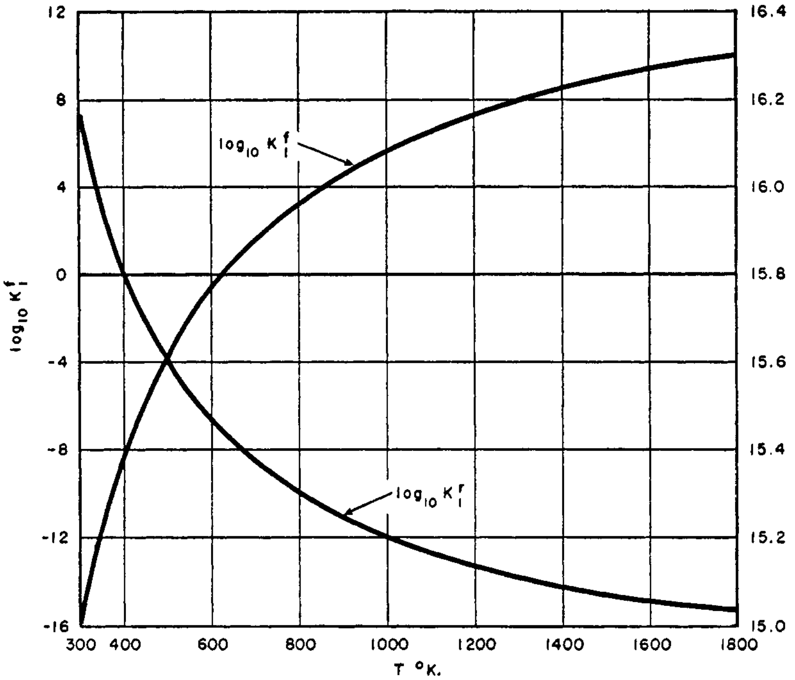

FIG. 6. Logs for the specific rates in the equation $d[\mathrm{Br}]/dt = k_2^f[\mathrm{Br}_2]^2 - k_2^r[\mathrm{Br}]^2[\mathrm{Br}_2]$; *cf.* table 18.

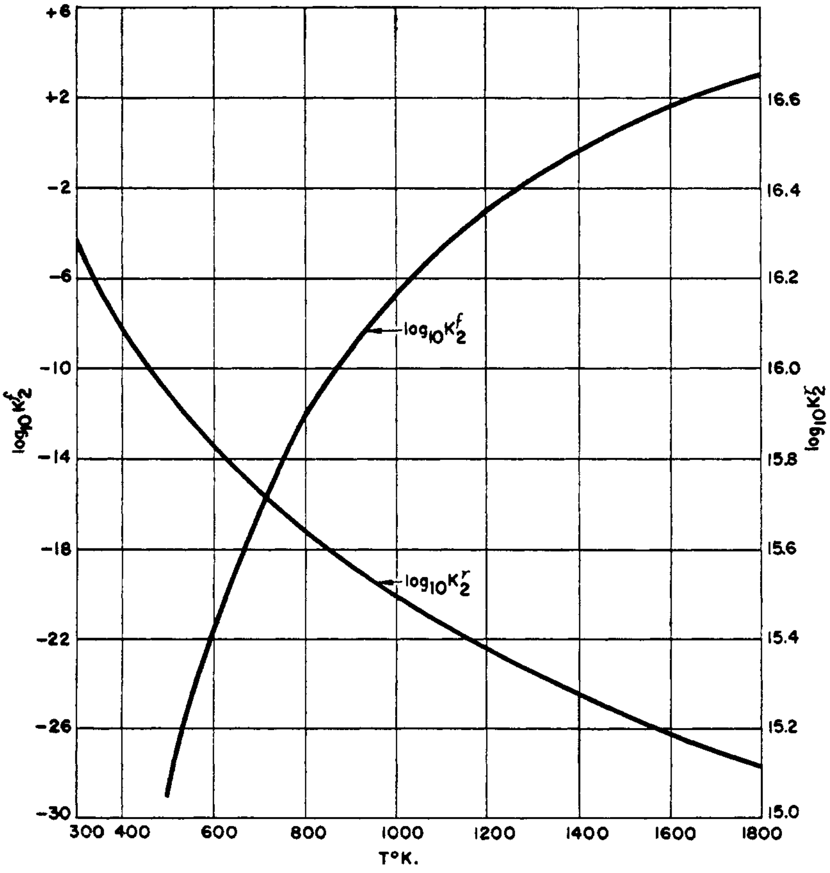

FIG. 7. Logs for specific rates in the equation $d[\mathrm{H}]/dt = k_2^f[\mathrm{H}_2][\mathrm{X}] - k_2^r[\mathrm{H}]^2[\mathrm{X}]$; *cf.* table 18.

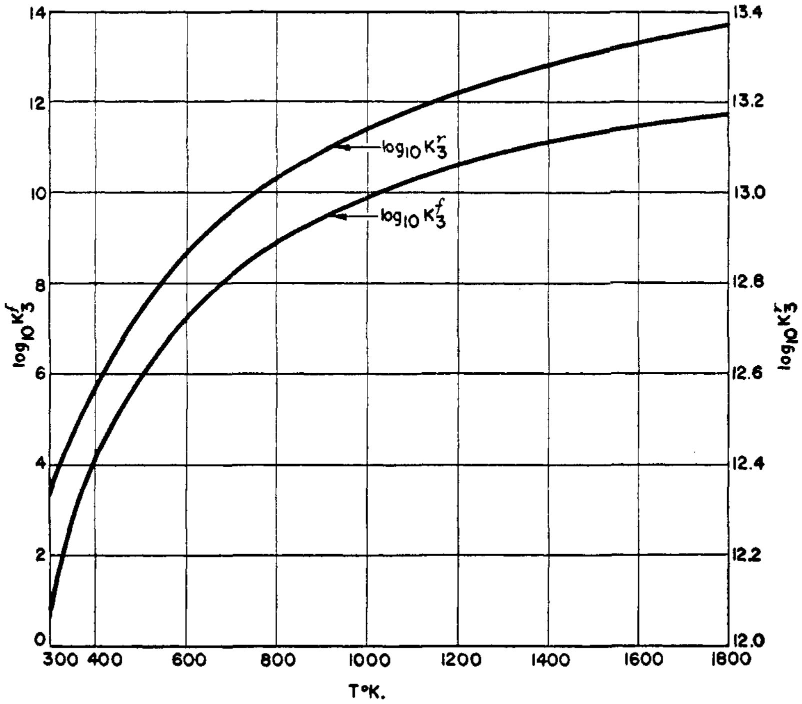

FIG. 8. Logs for specific rates for the equation $d[H]/dt = k_3^f[H_2][Br] - k_3^r[H][HBr]$; *cf* table 18.

A. EXPERIMENTAL TECHNIQUES FOR MEASURING TRANSPORT COEFFICIENTS

1. *Thermal conductivity*

Generally thermal conductivity is measured by heating a wire or other surface to a known temperature and determining the heat loss to a surrounding gas at some other known temperature. The surface loses heat by radiation, convection, and conduction. The major experimental difficulty—the reduction of the effects of convection—usually limits the accuracy of measurements of thermal conductivity to a few per cent.

2. *Diffusion coefficients*

In general, diffusion coefficients have been determined by measuring either (*a*) the amount of material transferred in a unit time across a carefully constructed boundary between two systems or (*b*) the rate of evaporation from a liquid surface with a known concentration gradient above it (74). As in measurements of thermal conductivity, the effects of convection generally have limited precision to a few per cent. Recently, very careful measurement of concentrations with an interferometer has yielded results reliable to a few tenths of a per cent (78). Unfortunately, interferometric techniques are limited to temperatures below about 100°C. In a fourth method a small gas source is inserted in a laminar stream and the rate of diffusion from this approximately point source is measured by a

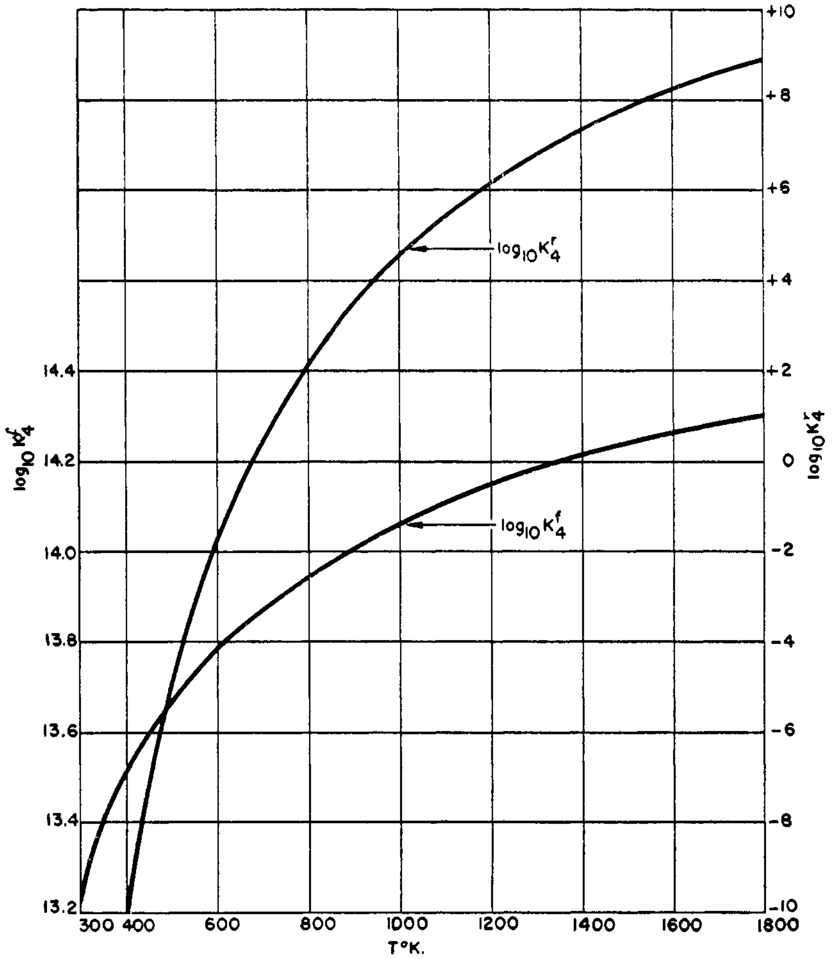

FIG. 9. Logs for the specific rates in the equation $d[Br]/dt = k_4^f[H][Br_2] - k_4^r[Br][HBr]$; *cf.* table 18.

sampling procedure (79). This technique is applicable at high temperature and has been used to study levels of turbulent diffusion in flames (78). By modifying this technique, it appears possible to derive diffusion coefficients to 1300°K. or higher with an accuracy approaching 1 per cent (79). It is hoped that in the near future this method will give direct experimental values for diffusion coefficients for the hydrogen–bromine system over an extended temperature range.

3. *Coefficient of viscosity*

Viscosity is not directly important in most flame studies, since it does not contribute appreciably to the kinetic energy of ordinary low-velocity flames.[28] However, viscosity data are of indirect value in estimating the other transport coefficients (*cf.* Section IV,B,1,c).

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[28] See reference 35: (a) pp. 206–9; (b) pp. 208–13; (c) pp. 215–22.

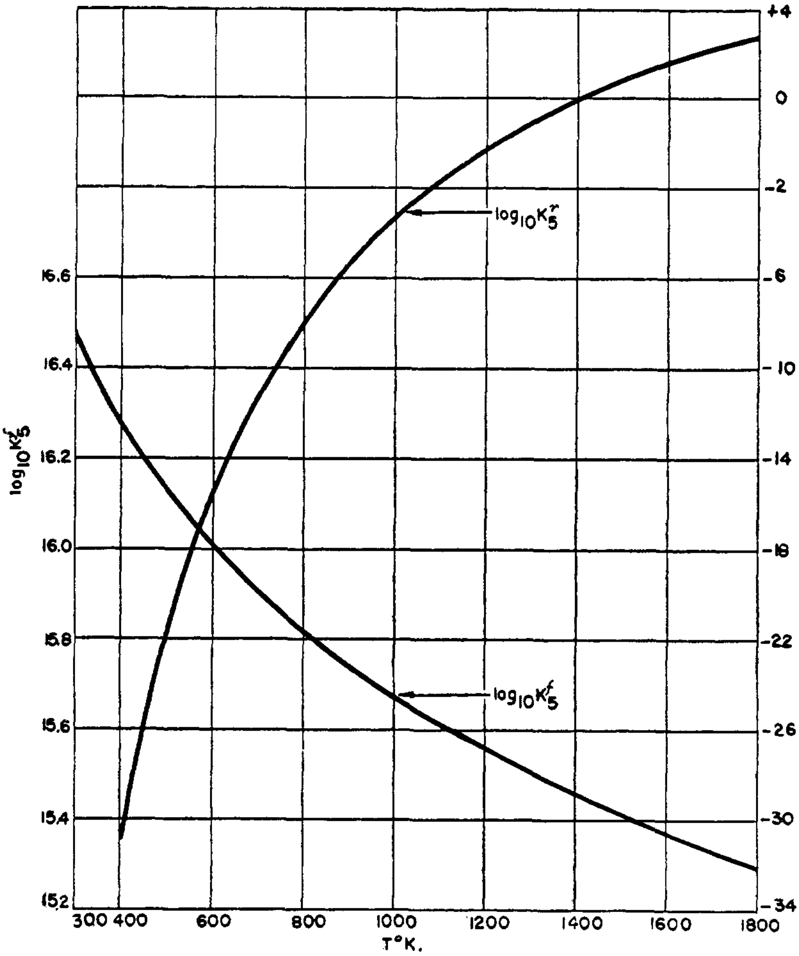

FIG. 10. Logs for specific rates in the equation d[HBr]/dt = k_5^f[H][Br][X] − k_5^r[HBr][X] *cf.* table 18.

Viscosity is a function of the momentum transport by molecules and is measured experimentally by studying flow through capillaries or measuring the drag on a moving surface. Accurate measurements require careful work and corrections for effects such as slip, flow, and curvature of the flow path (if coiled capillaries are used). Recent studies of mixtures over a 1000° temperature range (80) have verified the applicability of the Sutherland relation for viscosity to some complex systems.

$$\eta = \eta_0(T/T_0)^{\frac{3}{2}}(C + T_0)/(C + T) \tag{61}$$

B. THEORETICAL ESTIMATION AND EXTRAPOLATION OF TRANSPORT COEFFICIENTS

The intermolecular potential function for isolated molecular pairs defines the transport coefficients, the second virial coefficient, and the scattering of molecular beams. Therefore, if any one of these quantities can be experimentally measured, it can be used to determine the intermolecular potential function, and hence to calculate the desired transport property. In practice, it is necessary to assume that the potential can be described by some simple function involving arbitrary parameters which are determined by fitting experimental data. The two most popular models for spherically symmetric molecules are the Lennard–Jones 12-6 potential:

$$U(r) = 4\epsilon\left[-\left(\frac{r_0}{r}\right)^6 + \left(\frac{r_0}{r}\right)^{12}\right] \tag{62a}$$

and the modified Buckingham exponential-six potential:

$$U(r) = \frac{\epsilon}{1-(6/\alpha)}\left\{\frac{6}{\alpha}\exp\left[\alpha\left(1-\frac{r}{r_m}\right)\right] - \left(\frac{r_m}{r}\right)^6\right\}, \quad r \geqq r_m \tag{62b}$$

$$U(r) = +\infty, \quad r < r_m$$

where $U(r)$ = potential function (62c)
ϵ = depth of potential well
r = distance between centers of spherically symmetric molecules
r_0 = value of r at which $U(r)$ is zero, or, equivalently, the limiting value for the collision diameter as the velocity of approach tends to zero

The transport coefficients are related to these parameters through a set of collision integrals which contain the intermolecular potential in the integrand. If the potential parameters have been assigned by an empirical fit of data on one coefficient, then any other can be evaluated by interpolating in a set of tables constructed by numerical integration for a set of values of the parameters, with an accuracy of about 0.3 per cent (38).

The use of experimental data to determine the potential function is discussed in Section 1 and the derivation of the thermal conductivity and diffusion coefficients in Section 2.

1. Empirical determination of potential parameters

a. Second virial coefficient data

The P-V product can be expressed as a series in inverse powers of volume. The coefficient of V^{-n} in the expansion is a function of the simultaneous interaction of $(n + 1)$ molecules. Thus, the second virial coefficient, i.e., the coefficient of V^{-1}, can be used to determine the potential of interaction of two isolated molecules. However, since the second virial coefficient, B_1, must be measured by the first-order deviation from the ideal gas law,

$$B_1 = \lim_{P\to 0} V\left(\frac{PV}{RT} - 1\right) \tag{63}$$

P-V-T data accurate to within a few parts in 20,000 are frequently required to determine B_1 within 1 per cent or so.

b. Molecular beam scattering

Molecular beam scattering, the most direct method, gives potential constants with a precision of a few per cent (4, 5). Unfortunately, the detection problem has limited most studies to high-velocity beams corresponding to temperatures in the millions of degrees. Such hard collisions emphasize the repulsive part of the potential curve and therefore cannot yield parameters for the attractive part which plays a role in determining transport properties at flame temperatures. Recently tables have been prepared which give the parameters in the exponential-six potential by the numerical analysis of data from low-velocity beams (52a).

c. Transport coefficient data

Viscosity is the only transport property that has been studied over a sufficiently broad temperature range with sufficient precision to allow the evaluation of potential parameters. One of the first attempts to determine 12-6 parameters that would reproduce experimental viscosity data met several surprising successes[28a] and several failures.[28b] In favorable cases it was even possible to predict the viscosity of mixtures within 1 per cent or so.[28c]

Whalley and Schneider (81) reported that viscosity data should be accurate to 0.5 per cent and preferably to 0.1 per cent if the criterion of best-fit were to define the 12-6 parameters within narrow limits. Although table 19 shows that the parameter values depend on the method used to fit the data, within the range $kT/\epsilon = 1.2\text{–}3.0$ the fit of viscosity data was excellent and similar values for ϵ/k and r_0 were obtained from both virial and viscosity data. Simple gases, such as helium, carbon dioxide, nitrogen, oxygen, nitric oxide, and argon, showed a decrease in the apparent values of ϵ/k with increasing T. Thus, for helium the values varied from about 6° to 185°K. over the temperature range 15–1000°K. The upper temperature at which viscosity data could be fitted within the limits of experimental error by a single pair of parameters was about 500, 730, and 830°K. for nitrogen, oxygen, and argon, respectively. For carbon dioxide, ϵ/k from virial and viscosity data gave opposite trends with temperature. Despite the apparent inadequacy of the 12-6 model, Whalley and Schneider concluded that for simple gases such as the ones that they studied, a single choice of param-

TABLE 19

Dependence of 12-6 potential parameters upon the method used to fit viscosity data

Substance	Method		
	S/T curves	s curves	Initial guess with successive approximations
H_2	27.6	22.3	33.3
N_2	94	79	91.5
O_2	117	104	113.2
A	120	129	124
CO_2	216	216	190

The data of columns 1 and 2 are taken from Whalley and Schneider (81), who define and discuss the methods indicated by the column headings. The data of the last column are taken from Hirschfelder, Curtiss, and Bird (38).

eters from low-temperature data should be capable of predicting the viscosity up to about 1500°K. within an error of about 5 per cent. This apparent anomaly can be explained as follows by considering the theoretical equation for η, the coefficient of viscosity (38):

$$\eta = \frac{2.6693 \times 10^{-5}(MT)^{\frac{1}{2}}}{r_0^2} A(kT/\epsilon) \qquad (64)$$

In this equation $A(kT/\epsilon)$ is a comparatively slowly varying function of temperature. Thus if kT/ϵ were to vary over the enormous range of 0.3 to 400, $A(kT/\epsilon)$ would vary only by a factor of 5.8. If $\epsilon/k = 100$°K., then for this range of $kT/6$, $T^{\frac{1}{2}}$ would vary by a factor of 36.5. Note that from room temperature to 1500°K. the actual variation of kT/ϵ is only a factor of 4.

The use of viscosity data to determine parameters for the components of a hydrogen–bromine flame has been reasonably successful only for hydrogen (81). For bromine, the viscosity data could be reproduced by ϵ/k in the range 520–700°K. and r_0, 4.268 to 3.956 A. The latter values compare with viscosity-assigned r_0 for chlorine of 4.115 A. Existing data on hydrogen bromide cannot be fitted at all (35, p. 210). Since the data for hydrogen chloride and hydrogen iodide[29] both can be fitted, this is probably due to inaccuracy in the data.

2. Use of 12-6 parameters to estimate diffusion coefficients and thermal conductivity

Since, in general, transport coefficients and the second virial coefficient each have a different functional dependence on the intermolecular potential, each will predict somewhat different values for the parameters. The importance of these differences is discussed in the two following subsections.

a. Estimation of diffusion coefficients

Since ϵ and r_0 should be very similar for isotopes, recent experiments on the diffusion of isotopes offer a direct check upon the applicability of viscosity-assigned parameters to predict diffusion coefficients. Winn's experiments on isotopic diffusion (82) in several cases covered temperatures between −196°C. and 80°C. He obtained excellent agreement in the case of argon, deviations up to 5 per cent for neon, 10 per cent for nitrogen, 4 per cent for carbon dioxide, 10 per cent for oxygen, and 20 per cent for methane (at the lowest temperature). Winter (83) measured nitrogen, oxygen, and carbon dioxide at 273°K. and 318°K. His values for nitrogen and oxygen were different from Winn's and agreed with calculated values within 2 per cent. The discrepancy for carbon dioxide remained. It seems that viscosity parameters will produce the diffusion coefficients for such simple molecules within a few per cent at about room temperature.[30]

If viscosity studies are to be used to estimate diffusion coefficients of anything but isotopes, then an assumption must be made about the parameters for the

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[29] Note that in both reference 35 and reference 38 (Table 8.4-4, p. 567) the claim is made that hydrogen iodide cannot be fitted. However, reference 38 gives parameters for hydrogen iodide on p. 1112.

[30] For further discussion on diffusion measurements see reference 38, pp. 578–81.

different species. One of the most valuable accomplishments of the theory has been its prediction of diffusion coefficients using the very simple assumptions:[30]

$$r_{12} = (r_{11} + r_{22})/2;\ (\epsilon/k)_{12} = [(\epsilon/k)_{11}(\epsilon/k)_{22}]^{\frac{1}{2}} \tag{65}$$

The only data over a wide temperature range are for the diffusion of carbon dioxide and water into air from about room temperature to 1500°K. (47). The investigators found that the conventional formula:

$$D(T) = D(T_0)(T/T_0)^n \tag{66}$$

gave values that were too high when $n = 1.96$ and too low when $n = 1.5$ (the hard-sphere value). However, they could correlate their data with the empirical formula:

$$D(T) = CT^{\frac{3}{2}}/(C_0 + T) \tag{67}$$

The 12-6 model gives an excellent fit for their data for carbon dioxide (78) but a poor fit for the highly polar water molecule. The success for carbon dioxide leads to the hope that the 12-6 model may be reasonably successful in predicting diffusion coefficients (as well as coefficients of viscosity) for nonpolar molecules such as nitrogen, carbon dioxide, etc. up to temperatures as high as 1500°K.

Unfortunately, this is not the case for the components of a hydrogen–bromine flame. Whalley and Schneider (81) were unable to find reasonable 12-6 parameters which would reproduce the scant data on the diffusion of bromine. This failure can be attributed either to inaccuracy of the data or to the inapplicability of the 12-6 potential. Nevertheless, since the 12-6 model is as good as any other for handling the data which are of limited accuracy, it has been used to provide data for flame calculations.

b. Estimation of thermal conductivities

Viscosity-predicted 12-6 parameters do not give adequate estimates for thermal conductivity (35, p. 230). For example, errors of 5–15 per cent were found for carbon dioxide over the range 100–300°K. This has been attributed to the failure of the Eucken approximation, which incorrectly assumes a complete exchange between translational energy and internal degrees of freedom. If this explanation is correct, then viscosity parameters should predict accurately the thermal conductivities for monatomic gases which lack internal degrees of freedom. Over a temperature range of −186°C. to 306°C. the only deviations exceeding 2 per cent for the inert gases occurred with a single datum for krypton and some data for helium which were considered less reliable experimentally (42). This explanation has also been tested by comparing the dimensionless ratio of the thermal conductivity to the product of the viscosity and heat capacity:

$$f = \lambda/(\eta C_v) \tag{68}$$

where λ = thermal conductivity in cal. cm.$^{-1}$ sec.$^{-1}$ deg.$^{-1}$
η = viscosity in poises
C_v = heat capacity at constant volume in cal. deg.$^{-1}$ g.$^{-1}$

Chapman (18) shows that for molecules without internal degrees of freedom which repel according to the law of r^{-s}, f should be approximately independent of temperature and should have a value varying between 2.5 ($s = 5$) and 2.522 ($s = \infty$). In agreement with this prediction the inert gases show no appreciable temperature dependence for f (42). Conversely, Grilly (29) found that for gases such as carbon monoxide, oxygen, nitric oxide, carbon dioxide, methane, and nitrous oxide, there is no correlation between the temperature variation for f found experimentally and that predicted by the Eucken approximation. In disagreement with Kannuluick and Carman, he claimed that f for helium does vary with temperature. Since the data of Kannuluick and Carman (42) on thermal conductivity agree well with the values of Johnston and Grilly, the discrepancy must be due to the η values used.

The Eucken approximation predicted well the thermal conductivity of only H_2 (*cf.* table 20). Therefore, the 12-6 potential model seems to be of doubtful value in estimating the thermal conductivity of bromine and hydrogen bromide and empirical extrapolations have been used.

C. EMPIRICAL REPRESENTATIONS FOR TRANSPORT COEFFICIENTS

Extrapolation of experimental data for use in flame calculations requires that the transport coefficients be known as explicit functions of temperature. Various empirical representations are discussed in the following subsections.

1. Thermal conductivity of pure gases

Keyes (46) has given analogous equations for correlating thermal conductivity and viscosity data of pure gases:

$$\lambda = C_0 T^{\frac{1}{2}}/[1 + CT^{-1} \exp[-(C_1 \ln_e 10)/T] \tag{69}$$

where λ = thermal conductivity in cal. cm.$^{-1}$ sec.$^{-1}$ deg.K.$^{-1}$
T = absolute temperature (in degrees Kelvin)
C, C_0, C_1 = empirical constants

For air, constants (determined by empirically fitting data over the temperature range −183° to 300°C.) reproduced recently measured data up to temperatures of about 2500°K. to within about 3 per cent. Keyes observed that for air, the vibrational energy remains small relative to the sum of rotational and translational energies, even at 2500°K. Conversely, for methane, no single set of constants sufficed to represent the data up to 800°K. At that temperature, the vibrational energy for methane exceeds the total energy of translation and ro-

TABLE 20

T, °K	100	200	273	300
10^7 λ (H_2), calculated	1618	3053	3878	4140
10^7 λ (H_2), experimental	1625	3064	3965	4227

The calculated values of thermal conductivity are based on the viscosity-assigned 12-6 parameters for H_2. The units are cal. cm.$^{-1}$ sec $^{-1}$ (°K.)$^{-1}$ The data are from reference 38, Table 8, 4–10, p. 574.

tation. Presumably the adequacy of the representation decreases when the relative contribution of vibrational energy increases.

Keyes' equation is a modification of the Sutherland equation for viscosity:

$$\eta = C_0 T^{\frac{1}{2}}/(1 + CT^{-1}) \tag{70}$$

The viscosity of hard spheres whose attraction varies with an inverse power of distance approaches this equation when the temperature is sufficiently high that only first-order terms in attraction need be considered. At lower temperatures, where the attraction is larger, the Sutherland equation is expected to underestimate the viscosity (18, pp. 223–6). Keyes selected a function which increases the predicted viscosity at low temperatures and approaches the Sutherland form as T increases.

2. Thermal conductivity of mixtures

At the present there is no rigorous method of calculating the thermal conductivity of a mixture of polyatomic gases (38, p. 536). Even the empirical relation between the thermal conductivity of the mixture and the thermal conductivities of the pure components is complicated. In the case of the binary mixture of nitrogen and carbon dioxide, the deviation from the linear composition rule

$$\lambda \text{ (mixture)} = \sum_i X_i \lambda_i \tag{71}$$

changes sign as the temperature is varied (46, p. 20).

Since present data on thermal conductivities of the pure components are so inadequate, the simple linear composition of equation 71 is recommended for the hydrogen–bromine system.

3. Binary diffusion coefficients

a. For gases which obey the 6-12 potential when $(kT/\epsilon) \geqslant 3$

The binary diffusion coefficient for a pair of gases which interact according to the 6-12 potential is given by

$$D_{12} = \frac{0.00263\sqrt{T^3(M_1 + M_2)/2M_1M_2}}{Pr_{12}^2\,\Omega_{12}^{(1,1)*}} \tag{72}$$

where D_{12} = diffusion coefficient, in cm.^{2} sec.$^{-1}$

M_1,M_2 = gram-molecular weights

T = temperature, in °K.

P = pressure in atmospheres

$\Omega_{12}^{(1,1)*}$ = reduced average collision integral for the Lennard–Jones potential; this is a function of kT/ϵ_{12}

TABLE 21

Correlation of binary diffusion coefficients by equation 74

Gas Pair	Temperature	D_{12} (calculated)	D_{12} (experimental)
	°*K*.	*cm.*^{2} *sec.*$^{-1}$	*cm.*^{2} *sec.*$^{-1}$
Argon–helium	273	0.61	0.64
Nitrogen–hydrogen	273	0.65	0.67
Nitrogen–carbon dioxide	273	0.140	0.144
Carbon monoxide–ethylene	273	0.143	0.116
Methane–air	273	0.194	0.196
Carbon dioxide–air	273	0.140	0.138
Hydrogen–nitrous oxide	273	0.57	0.54
Nitrogen–ethylene	298	0.166	0.163
Nitrogen–ethane	298	0.153	0.148
Hydrogen–methane	298	0.72	0.73
Hydrogen–butane	430	0.84	0.76

ϵ_{12}, r_{12} = Lennard–Jones parameters for the interaction between gases 1 and 2

Westenberg (78) found that for $(kT/\epsilon_{12}) \geqslant 3$ he could represent the collision integral by the empirical equation

$$\Omega_{12}^{(1,1)*} = a(kT/\epsilon_{12})^b \tag{73}$$

where $a = 1.12$ and $b = -0.17$. For work in flames, many gases are likely to be in this range. Therefore, the empirical representation of the binary diffusion coefficient of equation 72 is

$$D_{12} = \frac{0.00166T^{1.67}\sqrt{(M_1 + M_2)/M_1M_2}}{Pr_{12}^2(\epsilon_{12}/k)^{0.17}} = AT^{1.67} \tag{74}$$

Table 21 compares experimental values at atmospheric pressure and low temperature with values calculated by the empirical formula (given in equation 74), using equation 65 for r_{12} and $(\epsilon/k)_{12}$ and viscosity-assigned values for r_i and ϵ_i. Agreement at high temperatures would be poorer.

Since lack of experimental data and of a better method of estimating transport coefficients has forced us to use estimates based on the 6-12 potential and viscosity-assigned parameters, equation 74 is recommended as a formula that will be consistent with the method of estimation whenever $kT/\epsilon_{12} \geqslant 3$. It should be reëmphasized that the 6-12 representation is known to be inadequate for bromine (81).

b. Alternative empirical formula

The preceding formula cannot describe the behavior of the components of the hydrogen–bromine system to which the 6-12 potential does not apply and was recommended only because at the present time the only estimates for the diffusion coefficients are based on that model. A two-parameter equation has been successfully used to represent the data for the diffusion of the polar water molecule into air over the range 290–1470°K. (47).

$$D_{\beta\gamma}(T) = d_{\beta\gamma}T^{3/2}/(1 + d^{0}_{\beta\gamma}T^{-1}) \tag{75}$$

This Sutherland type formula should be considered as a possible representation when actual experimental data become available. Even now it is being used in flame calculations, since the successful representation of data for the polar water molecule suggests that its functional form may perhaps be applicable to the components of a hydrogen–bromine flame that do not obey the 6-12 potential.

D. ESTIMATION OF PARAMETERS IN EMPIRICAL FORMULAE FOR THE TRANSPORT COEFFICIENTS

1. *Thermal conductivity of pure substances*

a. Hydrogen[31]

Keyes (46) reviewed existing data and selected best values over the temperature range 90–595°K. He fitted equation 69 to these values to obtain the constants:

$$C_0 = 3.760 \times 10^{-5},\ C = 166.0,\ C_1 = 10 \tag{76}$$

b. Hydrogen bromide

Franck (25) studied the thermal conductivity of hydrogen bromide over the temperature range 193–582°K. As a check on the general quality of his data, his values for nitrogen and for carbon dioxide were compared with values interpolated from Keyes' tables (46). Below about 200°K. Franck and Keyes agree. As the temperature increases, Franck's values fall increasingly below those of Keyes, until at about 600°K. they are 8 or 9 per cent lower. On the assumption that Keyes' values were more reliable, Franck's were adjusted, as shown in table 22.

The adjusted values were correlated by Keyes' equation 69, using the constants:[32]

$$C_1' = \ln_e 10C_1 = 122;\ C_0 = 1.32 \times 10^{-3};\ C = 4.94 \times 10^{+5} \tag{77}$$

For these parameters and for flame temperatures less than 2000°K. the equation for the thermal conductivity of hydrogen bromide can be approximated with less than 0.5 per cent error by the simple form:

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[31] Recently an even more thorough critical review of thermal conductivity data on hydrogen has been published (77).

[32] The data were fitted empirically by the following steps: (*1*) choose a value of C_1; (*2*) compute C_0, C using data at two temperatures; (*3*) repeat steps 1 and 2 for another choice; (*4*) for the final choice of C_1, readjust C_0 and C to eliminate apparent trend in the deviation with temperature.

TABLE 22

Thermal conductivity of hydrogen bromide

T	Experimental Values $\lambda \times 10^5$		Calculated Values $\lambda \times 10^5$	Per Cent Deviation
	(a)	(b)		
°*K.*	*cal. cm.*$^{-1}$ *sec.*$^{-1}$ *deg.*$^{-1}$	*cal. cm.*$^{-1}$ *sec.*$^{-1}$ *deg.*$^{-1}$	*cal. cm.*$^{-1}$ *sec.*$^{-1}$ *deg.*$^{-1}$	
193	1.41	1.41	1.347	−4.3
275	1.79	1.81	1.897	+4.8
393	2.87	2.96	2.837	−4.2
475	3.32	3.55	3.572	+0.6
495	3.46	3.70	3.760	+1.6
582	4.31	4.71	4.620	−1.9
				2.9 (av.)

Column (a) gives Franck's data (25); column (b) gives the values adjusted in the way discussed above. The calculated values correspond to equations 69 and 77.

$$\lambda(T) = dT^{3/2} \exp\,(+C_1'/T)$$
$$d = C_0/C = 2.67 \times 10^{-9} \tag{78}$$

At temperatures greater than 373°K. this equation can in turn be approximated with less than 6 per cent error by the form

$$\lambda(T) = d[T^{3/2} - C_1'T^{1/2}] \tag{79}$$

c. Bromine

For bromine there is only a single datum at a single temperature (25):

$$\lambda(276°\text{K.}) = 1.03 \times 10^{-5} \text{ cal. cm.}^{-1} \text{ deg.}^{-1} \text{ sec.}^{-1} \tag{80}$$

Both the fact that the thermal conductivity for bromine is less than that for hydrogen bromide and the fact that the Lennard–Jones ϵ/k is greater for bromine than for hydrogen bromide (*cf.* table 23) suggest that for bromine the parameter C in equation 77 will probably be larger for bromine than for hydrogen bromide. Therefore, the simpler two-parameter equation 78 should also give a reasonable temperature dependence for $\lambda(Br_2)$. Since there is no basis for any more quantitative estimate of the parameter C_1', the value for hydrogen bromide has been used for bromine, and the parameter d has been determined from the sole measured value:

$$d = 1.44 \times 10^{-9};\ C_1' = 122 \tag{81}$$

d. Atomic species

There are no data on the thermal conductivity of either hydrogen or bromine atoms. The mole-fraction of hydrogen atoms is so low that it cannot contribute significantly to the thermal conductivity. However, in a flame produced by a fuel

TABLE 23

Lennard-Jones parameters for the gases of table 24

Gas	(ϵ/k)	r_0	Gas	(ϵ/k)	r_0
	°K.			°K.	
Bromine	520	4.268	Hydrogen	33.3	2.968
Argon	124	3.418	Carbon dioxide	190	3.996
Methane	137	3.882	Nitrogen	91.5	3.681
Hydrogen chloride	360	3.305	Hydrogen bromide	342	3.50

Sources of data: Values for all substances except hydrogen bromide were taken from Table 1-A on pp. 1110–13 of reference 38. Since the existing data on the viscosity of hydrogen bromide cannot be correlated with this model (*cf.* Section IV,B,1,c), the parameters were estimated as follows: Proceeding from the observations

$$r_0(Cl_2)/r_0(HCl) = 1.245$$

and

$$r_0(I_2)/r_0(HI) = 1.208$$

it seems reasonable to suppose that

$$r_0(HBr) \cong r_0(Br_2)/1.22$$

The ϵ/k was taken to be the mean of the values ϵ/k(HI) and ϵ/k(HCl).

TABLE 24

Comparison of calculated with experimental binary diffusion coefficients, $D_{\beta\gamma}$

Pair		T	$D_{\beta\gamma}$ Experimental	$D_{\beta\gamma}$ Calculated	Per Cent Error
β	γ				
		°K.			
Br_2	A	288	0.085	0.082	−4
Br_2	CH_4	288	0.156	0.105	−33
Br_2	HCl	287	0.077	0.066	−14
Br_2	H_2	288.5	0.56	0.50	−11
Br_2	CO_2	288.5	0.085	0.061	−28
Br_2	N_2	288	0.132	0.095	−28
para H_2	H_2	273	1.285	1.234	−4
		85	0.172	0.166	−3
HBr	DBr	295	0.079	0.078	−1

The values are for P = 1 atm. in the units of cm.^{2} sec.$^{-1}$ Sources of data: (*a*) Br_2-N_2 (49). This value is somewhat uncertain. The diffusion coefficient that the authors reported for the pair Br_2-H_2 was altered about 7 per cent in a later study (50). Unfortunately they did not repeat the measurement on Br_2-N_2. (*b*) $Br_2-\gamma$ ($\gamma \neq N_2$) (50). (*c*) para-H_2-normal H_2 (30). (*d*) HBr-DBr (13).

gas of 50 mole per cent hydrogen and 50 mole per cent bromine, the mole-fraction of bromine atoms appears to go as high as 0.05–0.10 (17).

2. Thermal conductivity for the gas mixture

The simple linear composition rule of equation 71 has been suggested for estimating the thermal conductivity of the gas mixture.

In previous flame calculations a very poor representation was adopted for the sake of simplicity. The thermal conductivity of the flame produced by a fuel of 50 mole per cent hydrogen and 50 mole per cent bromine was estimated at the hot and cold boundaries, and a linear function of temperature was used for intermediate points.

TABLE 25

Calculated values of binary diffusion coefficients of the hydrogen–bromine system

β	γ	$D_{\beta\gamma}(373°K.)$	$D^{\circ}_{\beta\gamma}(1500°K.)$
		cm.² sec.⁻¹	*cm.² sec.⁻¹*
Br	Br_2	5.88×10^{-2}	8.47×10^{-1}
H	H_2	2.53×10^{0}	$2.55 \times 10^{+1}$
Br_2	H_2	7.51×10^{-1}	7.99×10^{0}
Br_2	HBr	7.90×10^{-2}	1.08×10^{0}
H_2	HBr	6.65×10^{-1}	8.53×10^{0}

The $D\beta\gamma$ at $P = 1$ atm. were computed using the Lennard-Jones parameters of table 23.

TABLE 26

Parameters for equation 75 for $D_{\beta\gamma}(T)$

β	γ	$d_{\beta\gamma} \times 10^5$	$d^{\circ}_{\beta\gamma} \times 10^{-2}$
Br	H	*21.7*	*1.77*
	Br_2	*1.97*	*5.26*
	H_2	*15.6*	*1.77*
	HBr	*2.81*	*4.49*
H	Br_2	*21.7*	*1.77*
	H_2	*47.9*	*1.36*
	HBr	*25.8*	*3.64*
Br_2	H_2	*15.4*	*1.77*
	HBr	*2.42*	*4.49*
H_2	HBr	*18.3*	*3.64*

Since there are no data on the potential parameters of the free atoms. the expected large difference between the atomic and molecular force fields has been ignored and the same ϵ/k and r_0 have been used for the atom X and the molecule X_2.[33] Therefore the binary diffusion coefficients involving X are related to those involving X_2 by the following mass corrections:

$$d_{Br,H_2} = 1.01\, d_{Br_2,H_2};\ d_{Br,HBr} = 1.16\, d_{Br_2,HBr}$$
$$d_{Br,H} = 1.41\, d_{Br_2,H_2};\ d_{H,Br_2} = 1.41\, d_{H_2,Br_2}$$
$$d_{H,HBr} = 1.41\, d_{H_2,HBr}$$

In previous flame calculations the values for (Br, Br_2), (H, H_2), (Br_2, H_2), (Br_2, HBr), (H_2, HBr) were rounded to the nearest integer with the exception of $d_{Br,Br_2} = 6 \times 10^{+2}$, $d_{H_2,HBr} = 3 \times 10^{+2}$. Then the rounded mass corrections used were:

$$d_{Br,H} = (3/2)\, d_{Br_2,H_2};\ d_{Br_2,H_2} = d_{Br_2,H_2}$$
$$d_{Br,HBr} = (5/4)\, d_{Br_2,HBr};\ d_{H,Br_2} = (3/2)\, d_{H_2,Br_2}$$
$$d_{H,HBr} = (3/2)\, d_{H_2,HBr}$$

All values are for $D_{\beta\gamma}$ at $P = 1$ atm., when the diffusion coefficients are in the units cm.² sec.⁻¹

TABLE 27

Values for the parameter in equation 74 for $D_{\beta\gamma}(T)$

β	γ	$A \times 10^6$
H	H_2	*12.7*
	Br_2	*5.53*
H_2	Br_2	*3.92*

The values of $D\beta\gamma(T)$ are in the units of cm.² sec.⁻¹ for $P = 1$ atm.

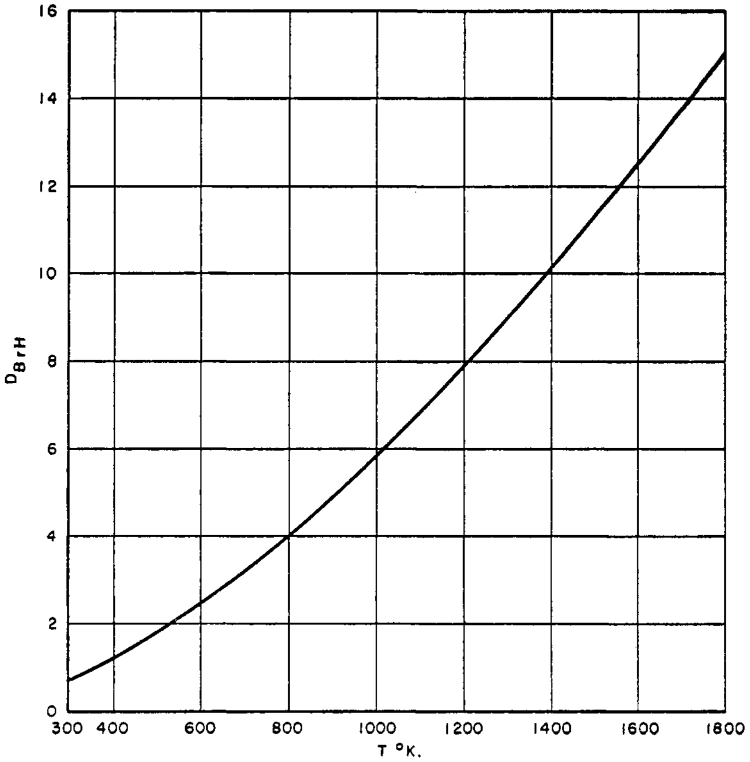

FIG. 11. Binary diffusion coefficient in cm.^{2} sec.$^{-1}$ at P = 1 atm.; *cf.* table 26

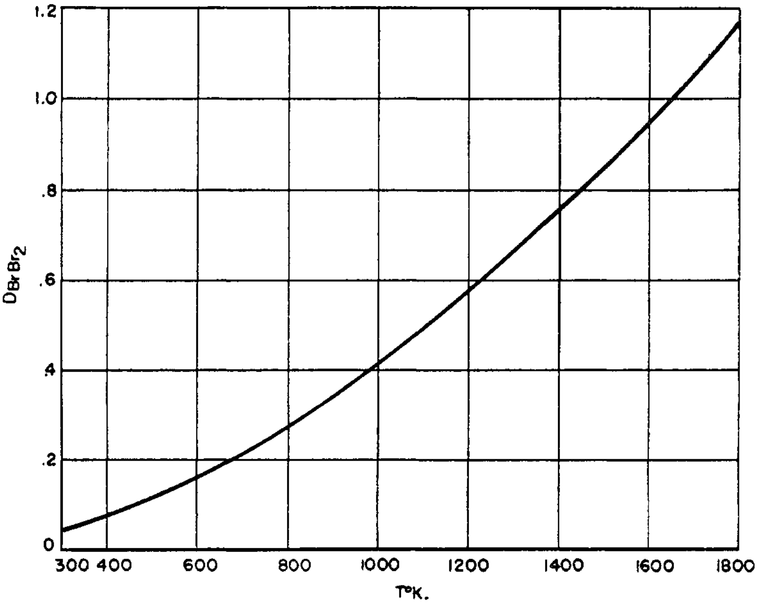

FIG. 12. Binary diffusion coefficient in cm.^{2} sec.$^{-1}$ at P = 1 atm.; *cf.* table 26

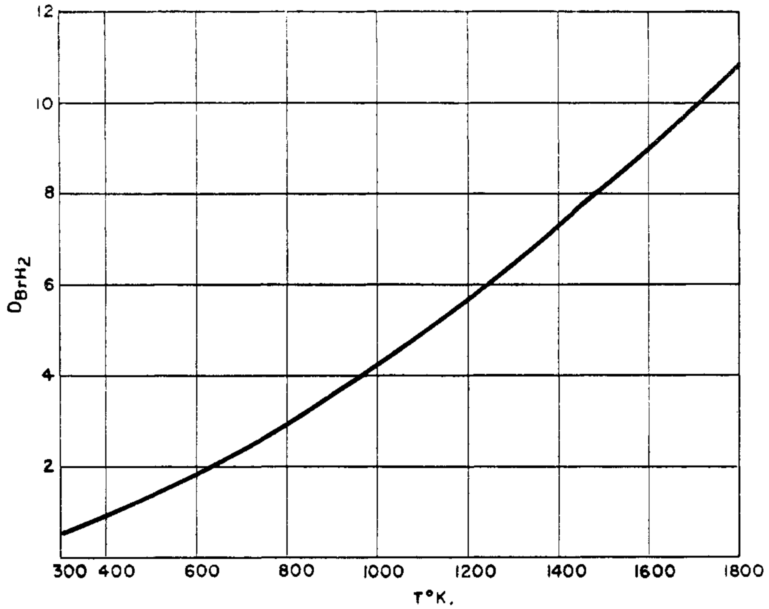

Fig. 13. Binary diffusion coefficient in cm.^{2} sec.$^{-1}$ at $P = 1$ atm.; *cf.* table 26

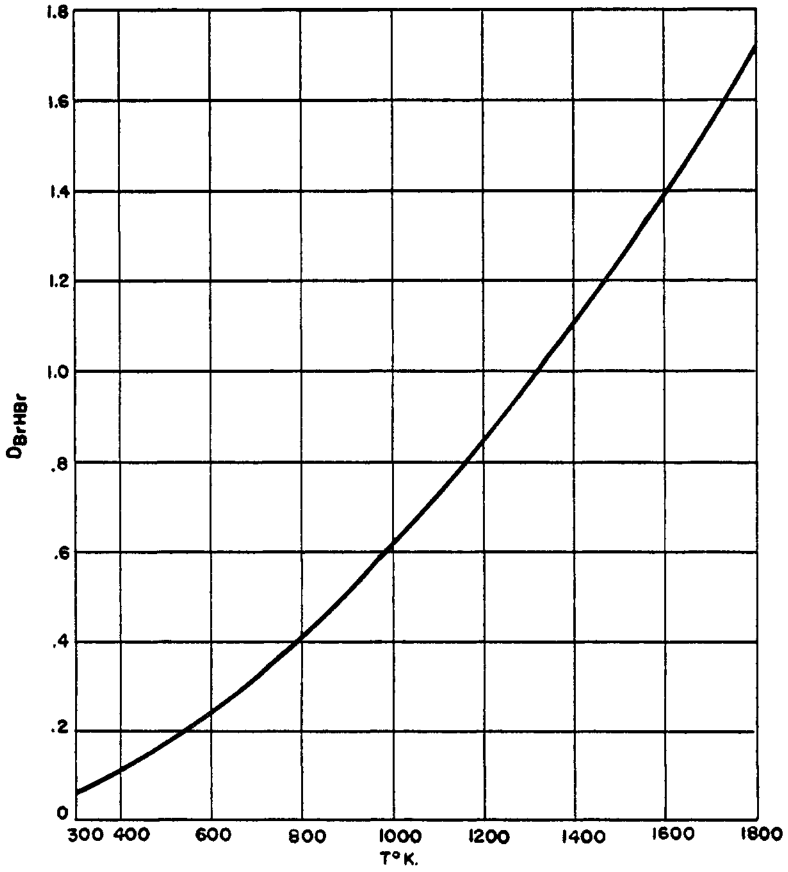

Fig. 14. Binary diffusion coefficient in cm.^{2} sec.$^{-1}$ at $P = 1$ atm.; *cf.* table 26

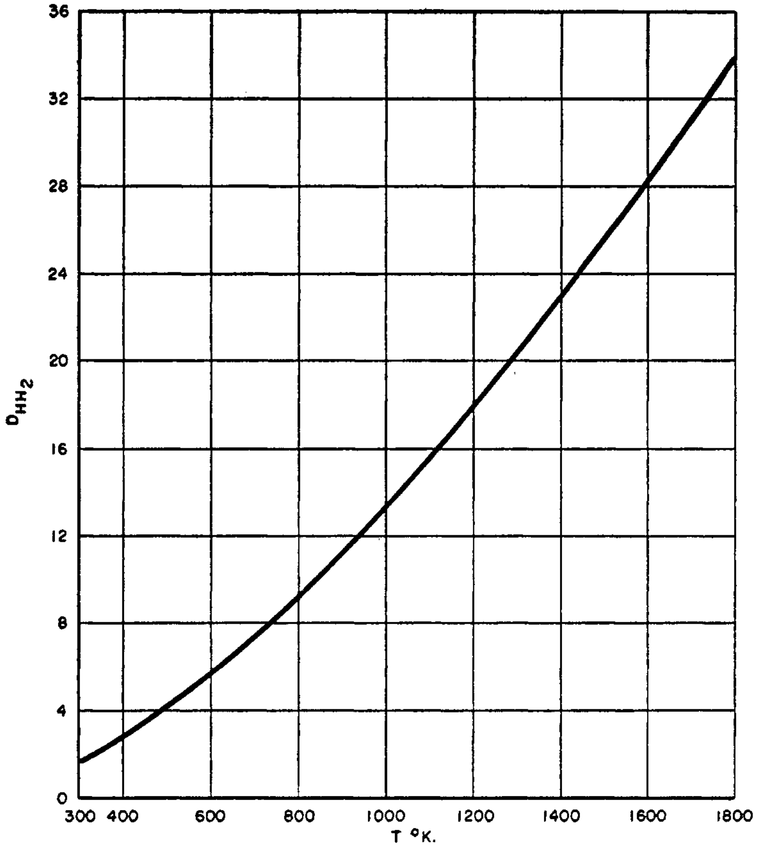

FIG. 15. Binary diffusion coefficient at $P = 1$ atm.; *cf.* table 26

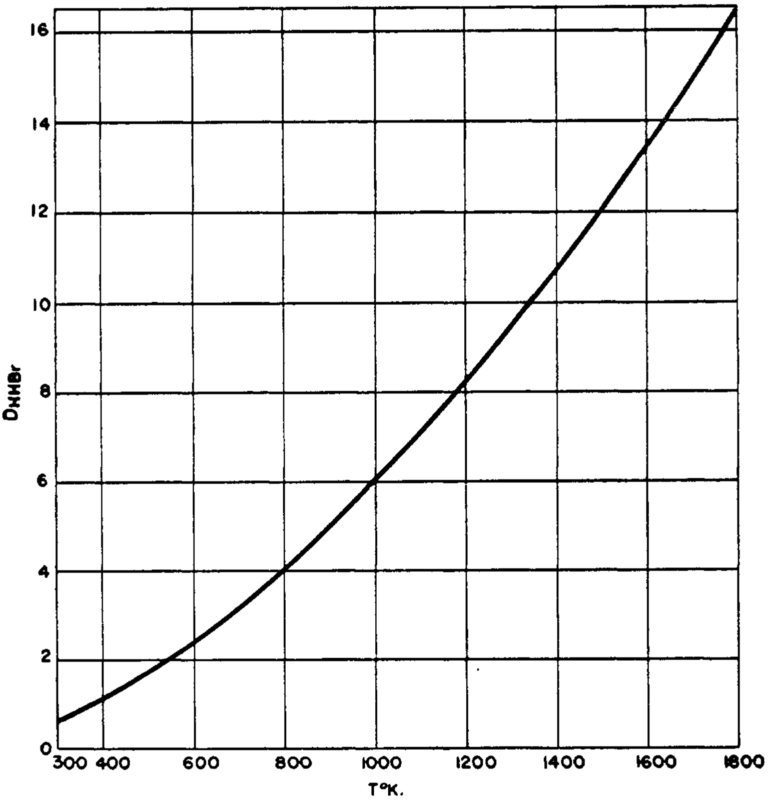

FIG. 16. Binary diffusion coefficient at $P = 1$ atm.; *cf.* table 26

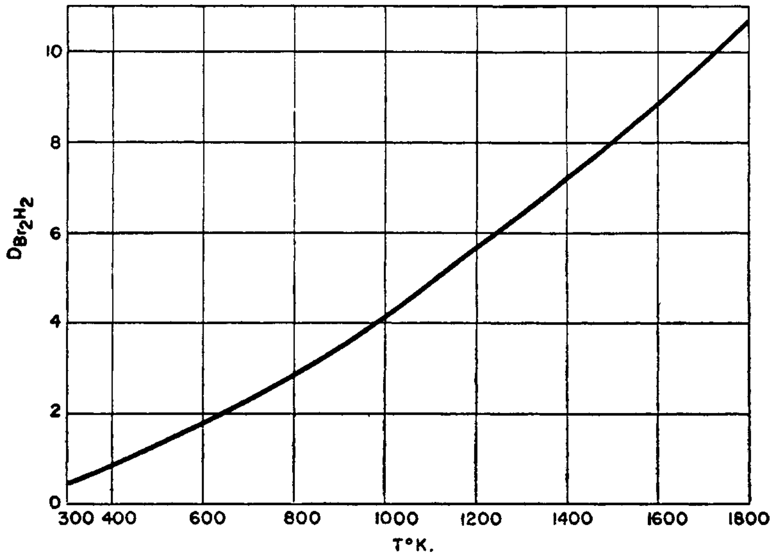

FIG. 17. Binary diffusion coefficient at $P = 1$ atm.; *cf.* table 26

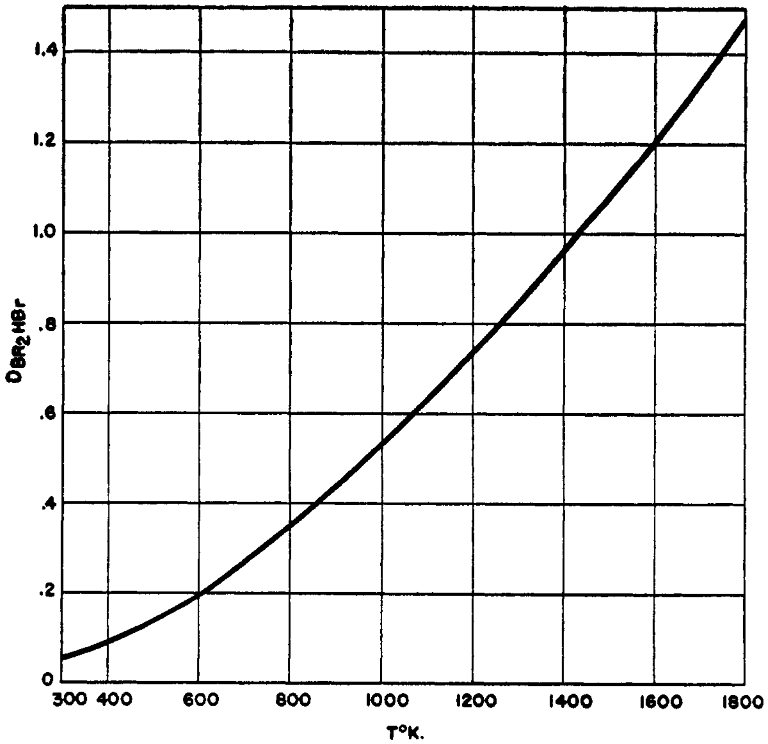

FIG. 18. Binary diffusion coefficient at $P = 1$ atm.; *cf.* table 26

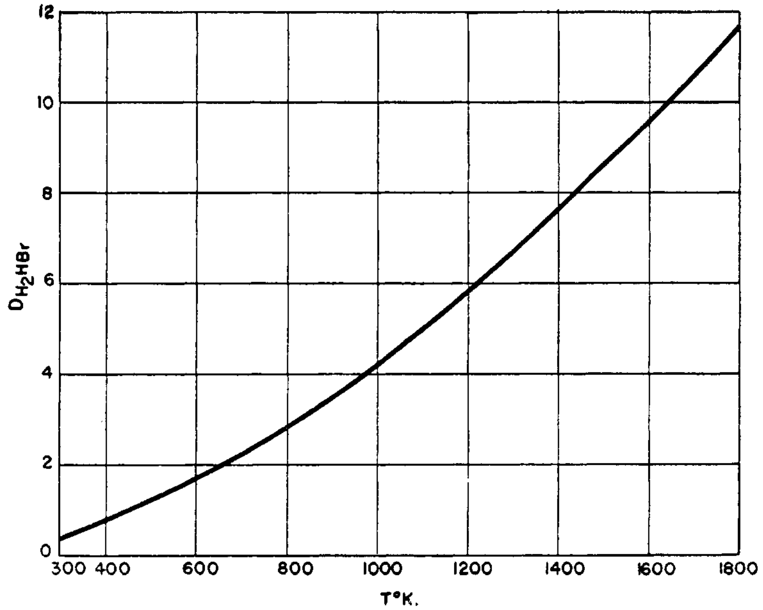

FIG. 19. Binary diffusion coefficient at $P = 1$ atm.; *cf.* table 26

3. Binary diffusion coefficients

The only experimental datum on the binary diffusion coefficients for the components of a hydrogen–bromine flame is one measurement for the pair bromine–hydrogen at 289°K. The coefficients had to be estimated from the kinetic theory of dilute gases with the spherically symmetric 12-6 potential function and the simple composition equation 65. Section IV,B,2 discusses the limitations of this model for the components of a hydrogen–bromine flame. Table 24 illustrates the order of uncertainty introduced by using this model at low temperatures. The error probably increases with temperature.

Since there are no data on the potential parameters of the free atoms, the expected large difference between the atomic and molecular force fields has been ignored and the same ϵ/k and r_0 have been used for the atom X and the molecule X_2.[33]

The parameter values of table 23 were used with tables of the collision integrals to compute the binary diffusion coefficients at two temperatures recorded in table 25. These values were in turn used to calculate the two parameters in equation 75 which are recorded in table 26.

Unfortunately, only the binary diffusion coefficients involving H or H_2 satisfy the condition $kT/\epsilon \gg 3$ for Westenberg's empirical equation (equation 74). The values for the parameter a for these pairs are recorded in table 27.

[33] Because of the uncertainty of the theoretical potential function governing the interaction of two hydrogen atoms, it did not seem worthwhile to use it as a basis for estimating the diffusion coefficient involving hydrogen atoms (51, 53, 54).

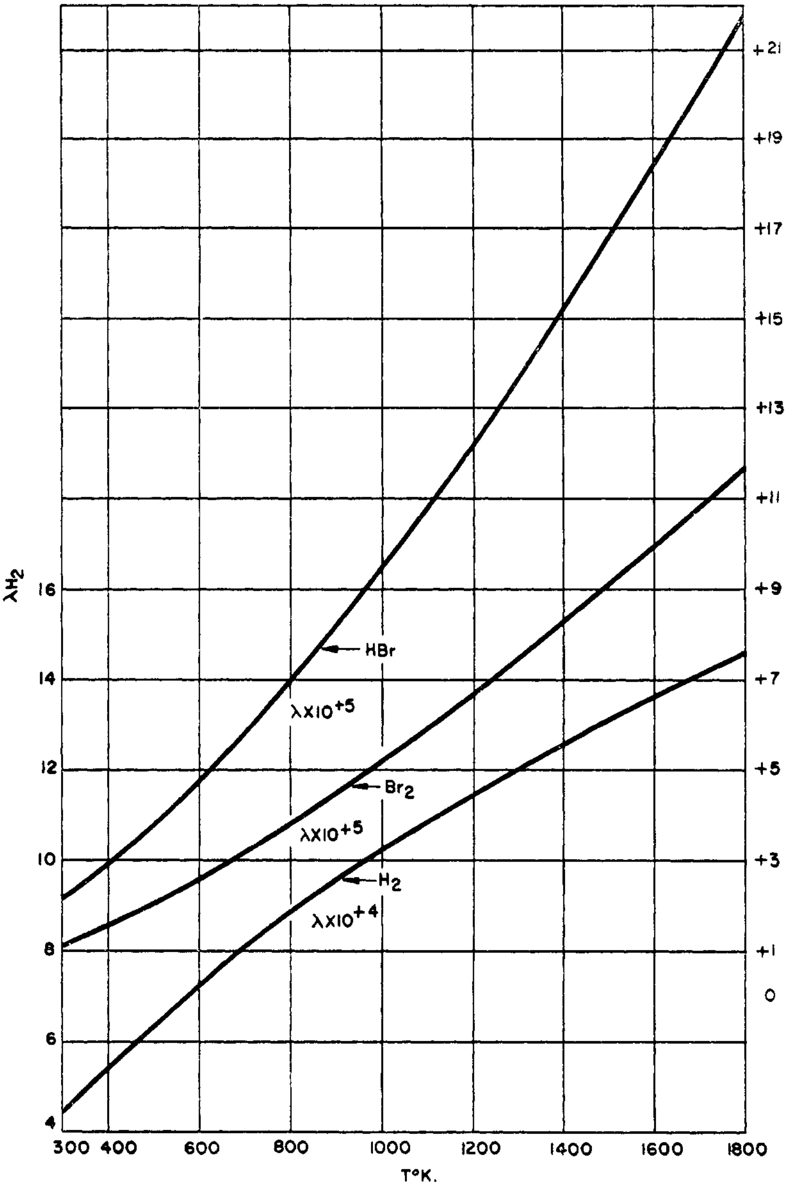

FIG. 20. Thermal conductivities, λ, in the units of cal. cm.$^{-1}$ deg.$^{-1}$ sec.$^{-1}$

V. SUMMARY

This review was undertaken to collect and evaluate the information required for a detailed theoretical analysis of the hydrogen–bromine flame. Although this is the best-known multicomponent flame system, much data had to be taken from conflicting information and untested extrapolations. The following summary presents an integrated view of the status of our knowledge.

A. THERMODYNAMIC PROPERTIES

The thermodynamic properties are the most satisfactory of the available data. There is information on all of the molecules of interest in this system and reliable estimates are given for the accuracy of the data. These data include energy, enthalpy, free energies, and heat capacities.

B. REACTION KINETICS[34]

The most important asset of this system from the standpoint of flame studies is the general agreement on the mechanism of the reaction and its relative

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[34] *Note added in proof:* Two important reports on the kinetics of the hydrogen–bromine reaction were presented at the 1957 meeting of the American Chemical Society in New York after this review had been submitted.

Theoretical calculations by Bunker and Davidson showed that the order of magnitude of the variation of the three-body recombination rates for iodine atoms could be predicted for various third bodies by assuming an equilibrium between an iodine atom and an X molecule,

$$\mathrm{X} + \mathrm{I} \rightleftarrows \mathrm{IX}$$

followed by a collision with a second iodine atom,

$$\mathrm{IX} + \mathrm{I} \rightarrow \mathrm{I_2} + \mathrm{X^*}$$

Because the important factor is the potential energy of interaction of X with I, and because the interaction of two iodine atoms is weaker, the other possible sequence

$$2\mathrm{I} \rightleftarrows \mathrm{I{-}I}$$

$$\mathrm{I{-}I} + \mathrm{X} \rightarrow \mathrm{I_2} + \mathrm{X^*}$$

would not reproduce the experimental data.

Another paper by Levy (48a) reported on a study of the kinetics of the hydrogen–bromine reaction in a flow system over the range 600–1400°K. Preheated samples of hydrogen and bromine were mixed by a jet mixer, and the reactive gases were cooled by striking a water-cooled cold-finger assembly in the furnace wall. Levy emphasized that his calculations are dependent upon rapid mixing of the hydrogen and bromine, and upon the subsequent rapid cooling of the reacting gases.

The reaction was followed by freezing out bromine and hydrogen bromide, separating them by vacuum condensation techniques, and measuring the gas volumes. As a measure of the consistency of Levy's data, one may take a sequence of thirty studies at 1250°. After omitting four values which showed a deviation greater than four times the average, the remaining twenty-six gave:

$$k_3^f = (1.48 \pm 0.58) \times 10^{10}$$

Levy reported the following results: (*a*) The reaction could be treated by the classical mechanism described by equations 17–20 and 23–26. Note especially that his data were interpreted (within the limits of their accuracy) by assuming that $k_4^f/2k_3^r = 4.2$ over the entire temperature range. This is the value reported from low-temperature studies by equation 26. (*b*) His data could be represented by the equation

$$k_3^f = 2.04 \times 10^{12} T^{1/2} \exp[-1.728 \times 10^4/RT]$$

(*c*) His quantitative results agreed roughly with the earlier low-temperature studies. Thus at 500°K., k_3^f computed from equation 29 is 9.27×10^5; from Pease's (56) equation, 6.80×10^5; from Levy's, 12.6×10^5. At 1400°K. the values were 1.22×10^{11}, 1.98×10^{11}, and 1.54×10^{11}, respectively.

simplicity. The reactions which are considered important in the hydrogen–bromine flame are:

(1) $Br_2 + X \rightleftarrows 2Br + X^*$
(2) $H_2 + X \rightleftarrows 2H + X^*$
(3) $Br + H_2 \rightleftarrows HBr + H$
(4) $H + Br_2 \rightleftarrows HBr + Br$
(5) $H + Br + X \rightleftarrows HBr + X^*$

Of these reactions, 2 and 5 are of only second-order significance. Although quantitative studies have been made on the rates of all reactions except reaction 5, all of the data are of limited accuracy. As the review has noted, kinetic data of low precision can be correlated within the limits of experimental accuracy by various temperature functions which predict extrapolated values differing by order of magnitude. Unfortunately, theory does not help, since it does not yet predict a unique temperature dependence. The necessity of extrapolation is probably the most serious limit on the use of kinetic data in flame studies. It is not yet known whether the rapid changes in the hydrogen–bromine flame will violate the basic assumption of conventional equilibrium theory of reaction kinetics that the formation of the activated species is rapid compared with the reaction itself. For some oxygen flames, this assumption has been shown to be false.

C. TRANSPORT PROPERTIES

The important transport properties for flame studies are the thermal conductivity and the diffusion coefficients. The information available is scattered, is of low precision, and does not cover the temperature range of interest.

1. Diffusion coefficients

The extrapolation of available diffusion coefficient data from the low temperatures at which they are available has been made using the rigorous kinetic theory and the 12-6 potential function in lieu of a more adequate model. The estimation of diffusion coefficients with potential constants derived from viscosity data and the composition equations has been reviewed and reported to give values with an accuracy of a few per cent for some nonpolar molecules, particularly those which are close to symmetric tops. The estimates are in general unsatisfactory for polar molecules and some nonspherical molecules such as Br_2. Nevertheless, these estimates had to be used in this review. At present there are neither experimental nor theoretical data on the transport properties of free radicals. In the absence of data, the difference between the force field of X and of X_2 has been ignored and the diffusion coefficients for X have been calculated from those for X_2, using simple mass corrections.

2. Thermal conductivity

Thermal conductivity data on hydrogen are good to a few per cent at temperatures up to about 600°K. The data on hydrogen bromide are less reliable and there is only a single datum for bromine. Data on bromine atoms would be desirable, since X_{Br} approaches the order of 0.1 in part of the high-temperature flame zone. Unfortunately there is no adequate theory for the extrapolation of thermal conductivity data to higher temperatures and empirical extrapolations had to be used. Since available theory does not predict the relation between the thermal conductivity of a mixture of polyatomic gases and that of the component species, a simple linear composition approximation (equation 71) was adopted.

D. CONCLUSIONS

Flame theory and experimental techniques have advanced to the point where direct comparison of theory and experiment should be possible. This review has sought to aid these studies by collecting the best available data and by pointing out its limitations. Theoretical calculations on the hydrogen–bromine flame using presently available data are important primarily as mathematical experiments, to discover the significance of various physical processes within the flame. More precise experimental studies of high-temperature kinetic and transport properties should be made, as a basis for the necessary detailed comparison of theory with experiment.

The authors gratefully acknowledge the importance of the assistance and encouragement given by Professor J. O. Hirschfelder in connection with the preparation of this review. Those who have had the pleasure of working with Professor Hirschfelder will appreciate what this has meant.

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APPENDIX A

BIMOLECULAR REACTION BETWEEN H_2 AND BR_2

Since a bimolecular mechanism seems to dominate the hydrogen–iodine reaction at ordinary temperatures, it is necessary to consider the possible significance of such a mechanism for the hydrogen–bromine reaction at elevated temperatures:

$$Br_2 + H_2 \rightleftarrows 2HBr \tag{82}$$

One form of the collision theory predicts that a specific rate constant will have the form

$$k = Z \exp(-\Delta E/RT) \tag{83}$$

where Z = collision number. Since this equation predicts the order of magnitude of the specific rate for the hydrogen–iodine reaction,[35] the frequency factor for the bimolecular hydrogen–bromine reaction was estimated from the value for $Z(H_2, I_2)$, given by fitting experimental kinetic data:

$$\begin{aligned} Z(H_2, Br_2) &\simeq Z(H_2, I_2) \left[\frac{r_{H_2} + r_{Br_2}}{r_{H_2} + r_{I_2}}\right]\left[\left\{\frac{M_{H_2} + M_{Br_2}}{M_{Br_2}}\right\}\left\{\frac{M_{I_2}}{M_{H_2} + M_{Ir_2}}\right\}\right]^{\frac{1}{2}} \\ &= 1.7 \times 10^{12} T^{\frac{1}{2}} \end{aligned} \tag{84}$$

Using the semiempirical estimate for the activation energy,[36]

$$\frac{d[HBr]}{dt} \simeq \{1.7 \times 10^{12} T^{\frac{1}{2}} \exp[-4 \times 10^4/RT]\}[H_2][Br_2] \tag{85}$$

where [ ] = units of mole cc.$^{-1}$ Although this review has reported that the conventional rate law should not be used to calculate rates at elevated temperatures, the quotient of the biomolecular rate to the conventional rate has been taken as a crude measure of the relative importance of the former. The ratio can be written in the form

$$R = C(T) X^{\frac{1}{2}}_{Br_2} \left\{1 + \frac{X_{HBr}}{4.2 X_{Br_2}}\right\} \tag{86}$$

Using the parameter values given in this review and a pressure of 0.983 atm., $C(T)$ has the following values: at 500°, 3.0×10^{-3}; at 1000°, 2.1×10^{-3}; at 1738°, 1.5×10^{-3}. An upper bound to the ratio R of equation 86 can be estimated as

$$\begin{aligned} R &= C(T) X^{\frac{1}{2}}_{Br_2} \left\{\frac{4.2 X_{Br_2} + X_{HBr}}{4.2 X_{Br_2}}\right\} \\ &< C(T) \left\{\frac{5.2}{4.2 X^{\frac{1}{2}}_{Br_2}}\right\} \end{aligned} \tag{87}$$

Assuming that X_{Br_2} in the flame > X_{Br_2} at equilibrium,

$$R(1738°) < 0.034 \tag{88}$$

Because R is relatively large, this crude estimate suggests, but does not insure, that the free-radical mechanism is more important than the bimolecular mechanism.

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[35] Kassel (43; *cf.* pp. 150–1) illustrates how crude a guess based on the collision theory must be. For the hydrogen–iodine reaction he shows that changing the temperature range to which the empirical rate is fitted changes the calculated value for the collision diameter by a factor of 4.

[36] Hirschfelder (34a) calculated ΔE = 41 kcal. from the rule that the energy of activation was approximately 0.28 times the strength of the broken bonds (*cf.* p. 653) and ΔE = 38 kcal., using n = 0.14 (*cf.* Table III, p. 652).

APPENDIX B

GLOSSARY OF SYMBOLS

C_1'...*cf.* equation 77

C, C_0...constants in an empirical equation for the binary diffusion coefficient (*cf.* equation 67), or
constants in an empirical equation for thermal conductivity (*cf.* equation 69), or
constants in an empirical equation for viscosity (*cf.* equation 70)

C_1...*cf.* equation 69

$(C_v)_\alpha$...*cf.* equation 1

$\overline{(C_v)}_\alpha$...*cf.* equation 1

$\Delta_i C_v$...*cf.* equation 1

$D_{12}, D_{\beta\gamma}$...the binary diffusion coefficient between species 1 and 2 [β and γ] in the units of cm.^{2} sec.$^{-1}$

E_0...the energy change accompanying reaction 1 at 0°K.

$\Delta_i E^\circ$...*cf.* equation 4

$\Delta_i F^\circ$...*cf.* equation 6

H_α°...the enthalpy of species α in its standard state (*cf.* equations 8, 9, and 10)

$K_i(T)$...*cf.* equation 1

$K_i(T_q)$...*cf.* equation 6

M_α...gram-molecular weight of species α

P...pressure

R...the ideal gas constant

T...absolute temperature

T_q...*cf.* equation 1

T_r...*cf.* equation 9

X...a symbol for various chemical species

X_α...the mole-fraction of species α

a...*cf.* equation 73

d...*cf.* equation 78

d_i...a constant in the empirical equation for the i^{th} equilibrium constant when concentrations are expressed in the units of moles cc.$^{-1}$ (*cf.* equation 4)

$d_{\beta\gamma}, \overset{\circ}{d}_{\beta\gamma}$...*cf.* equation 75

e_i...*cf.* equation 4

g_i^p, h_i^p...constants in the empirical equation for the specific rate for the forward ($p = f$) or the reverse ($p = r$) of the i^{th} reaction (cf. equation 11)

k...Boltzmann's constant

$k_{\text{A}}, k_{\text{Br}_2}, k_{\text{I}_2}, k_{\text{X}}$...specific rate for atom recombination with argon, bromine, iodine, or X as the third body

k_i^p...specific rate for the forward ($p = f$) or the reverse ($p = r$) of the i^{th} reaction (*cf.* equation 11)

$\Delta_i n$...*cf.* equation 5

r_0...*cf.* equation 62c

r_{12}...*cf.* equation 65

t...time

ϵ...parameter in empirical equations for the intermolecular potential function (*cf.* equation 62)

ϵ_{12}...*cf.* equation 65

γ...coefficient of viscosity

λ...coefficient of thermal conductivity in cal. cm.$^{-1}$ deg.$^{-1}$ sec.$^{-1}$