A Summary of Experimental Activation Energies of Elementary Reactions Between Hydrogen and the Halogens

J. Carrell Morris and Robert N. Pease

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ciency of various gases as third bodies. The order he finds agrees very well with the relative reactivities. The data of Senftleben and Hein,[17] however, are in definite disagreement with our theory, but the absolute rate for the recombin-

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[17] Senftleben and Hein, Ann. d. Physik **22**, 1 (1935).

ation of hydrogen atoms found by these authors is very much lower than that of Amdur or Steiner.

The method of potential energy surfaces thus provides us with a clear picture of homogeneous catalytic processes. It forms a convenient basis for a satisfactory discussion of the problems of energy transfer.


A Summary of Experimental Activation Energies of Elementary Reactions Between Hydrogen and the Halogens

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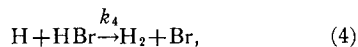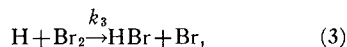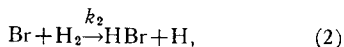
(Received July 22, 1935)

Existing experimental data on reactions between hydrogen and the halogens have been analyzed to give values of the activation energies of the intermediate reactions involved. These are compared with calculated values due to Eyring and Wheeler.

E VIDENCE has been accumulating over a period of years that reactions between molecules and free atoms may have appreciable activation energies. This evidence is in the main not direct, but must be deduced from considerations as to the most probable mechanism of reaction. In this paper the experimental evidence for reactions of hydrogen and the halogens is reviewed and tentative values of the activation energies are suggested. The reactions in question are of the types:

$$H+X_2 \rightarrow HX+X, \qquad X+H_2 \rightarrow HX+H,$$
$$H+HX \rightarrow X+H_2.$$
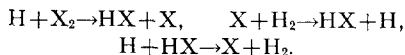
HYDROGEN-BROMINE REACTIONS

This reaction system has been quite thoroughly covered in both its theoretical and experimental aspects by Kassel in his *Kinetics of Homogeneous Gas Reactions*. However, newer numerical data have made possible more exact conclusions as to the individual reactions. The chain consists of the steps:

$$Br_2 \xrightarrow{k_1} 2Br, \tag{1}$$

$$Br+H_2 \xrightarrow{k_2} HBr+H, \tag{2}$$

$$H+Br_2 \xrightarrow{k_3} HBr+Br, \tag{3}$$

$$H+HBr \xrightarrow{k_4} H_2+Br, \tag{4}$$

$$Br+Br \xrightarrow{k_5} Br_2, \tag{5}$$

which lead to the theoretical expression:

$$\frac{d[HBr]}{dT} = 2k_2(k_1/k_5)^{\frac{1}{2}} \frac{[H_2][Br_2]^{\frac{1}{2}}}{1+k_4/k_3[HBr]/[Br_2]}.$$

From experimental researches by Bodenstein and Lind,[1] confirmed by Bach, Bonhoeffer and Moelwyn-Hughes[2] $2k_2(k_1/k_5)^{\frac{1}{2}}$ and k_4/k_3 have been determined. Since $k_5/k_1=K_D$, the dissociation constant of bromine, which is now well known, k_2 may be evaluated from the knowledge of $2k_2(k_1/k_5)^{\frac{1}{2}}$. The temperature coefficient of k_2 will give A_2, the activation energy of reaction (2). If the data of Gordon and Barnes[3] on K_D are used, both sets of results yield $A_2(Br+H_2)$ $=17.7$ Kg.Cals.
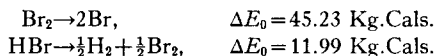
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[1] Bodenstein and Lind, Zeits. f. physik. Chemie **57**, 168 (1907).

[2] Bach, Bonhoeffer and Moelwyn-Hughes, Zeits. f. physik. Chemie **B27**, 71 (1934).

[3] Gordon and Barnes, J. Chem. Phys. **1**, 792 (1933).

From this value of A_2 theoretical reaction rates may be calculated and are found to agree quite well with observed values when reasonable molecular diameters $(3 \times 10^{-8}$ cm) are used.

Reaction (4), $H + HBr \rightarrow H_2 + Br$, is the reverse of the reaction just studied. The difference in activation energies between process (2) and the one just given may then be taken as the heat of reaction. This may be calculated thermochemically from the data of Gordon and Barnes,[3] who give these values:

$$Br_2 \rightarrow 2Br, \qquad \Delta E_0 = 45.23 \text{ Kg.Cals.}$$
$$HBr \rightarrow \tfrac{1}{2}H_2 + \tfrac{1}{2}Br_2, \qquad \Delta E_0 = 11.99 \text{ Kg.Cals.}$$

and from the recent work of Beutler,[4] who finds for hydrogen

$$H_2 \rightarrow 2H, \qquad \Delta E_0 = 102.68 \text{ Kg.Cals.}$$
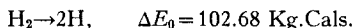
Proper combination of these leads to the result

$$H + HBr \rightarrow H_2 + Br, \qquad \Delta E_0 = -16.7 \text{ Kg.Cals.}[4a]$$

By direct subtraction a value, $A_4(H + HBr) = 1.0$ Kg.Cals., is obtained for reaction (4). This value of 1 kilogram calorie is in accord with the results of Cremer, Curry, and Polanyi,[5] who attempted to determine the rate of this reaction by passing atomic hydrogen into HBr. The reaction was too rapid for their measurements, which were made by means of the para to ortho-hydrogen conversion, so that they could only conclude that A_4 was less than 3.0 Kg.Cals.

The ratio k_4/k_3 was accurately determined by Bodenstein and Jung,[6] who found a value of 1/8.4 practically independent of temperature from 0° to 300°C, indicating that the A/RT terms are the same for reactions (3) and (4), for otherwise the ratio k_4/k_3 would vary with temperature. The constant factor of 1/8.4 may be ascribed to an "orientation factor," but whatever the explanation, it has no bearing on present reasoning. It follows for reaction (3) that $A_3(H + Br_2) = 1.0$ Kg.Cals.
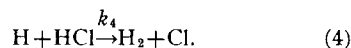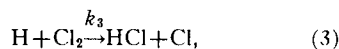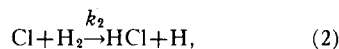
[4] Beutler, Zeits. f. physik. Chemie **B27**, 287–302 (1934).
[4a] Kassel gives −14.5 Kg.Cals. for the heat of this reaction. This seems to be an error.
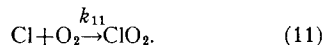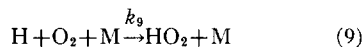[5] Cremer, Curry and Polanyi, Zeits. f. physik. Chemie **B23**, 445 (1933).
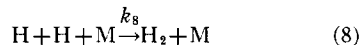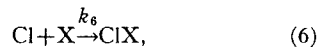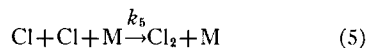[6] Bodenstein and Jung, Zeits. f. physik. Chemie **121**, 127 (1926).

HYDROGEN-CHLORINE REACTIONS

The attempt to evaluate some of the constants in the hydrogen-chlorine reaction is a more difficult task, since the reaction mechanism has not been as definitely settled as in the hydrogen-bromine reaction. The Nernst chain mechanism is well established, however.[7] According to this scheme the probable reactions in the photochemical hydrogen-chlorine combination are

$$Cl_2 + h\nu \xrightarrow{k_1} 2Cl, \qquad (1)$$

$$Cl + H_2 \xrightarrow{k_2} HCl + H, \qquad (2)$$

$$H + Cl_2 \xrightarrow{k_3} HCl + Cl, \qquad (3)$$

$$H + HCl \xrightarrow{k_4} H_2 + Cl. \qquad (4)$$

The chain-ending mechanisms may possibly be any of the following

$$Cl + Cl + M \xrightarrow{k_5} Cl_2 + M \qquad (5)$$

$$Cl + X \xrightarrow{k_6} ClX, \qquad (6)$$

$$H + X \xrightarrow{k_7} HX, \qquad (7)$$

$$H + H + M \xrightarrow{k_8} H_2 + M \qquad (8)$$

$$H + O_2 + M \xrightarrow{k_9} HO_2 + M \qquad (9)$$

$$H + O_2 \xrightarrow{k_{10}} HO_2 \qquad (10)$$

$$Cl + O_2 \xrightarrow{k_{11}} ClO_2. \qquad (11)$$

In this scheme X represents any foreign chain-breaker other than oxygen, such as the wall, or, with Bodenstein,[8] a volatile compound of silicon. M is a third body, either H_2, Cl_2 or HCl.

The most significant experiment toward the evaluation of activation energies in this series of

[7] For a complete discussion see Semenov, *Chemical Kinetics and Chain Reactions*, pp. 98–115.
[8] Bodenstein and Unger, Zeits. f. physik. Chemie **B11**, 253 (1931).

reactions was a direct determination by Rodebush and Klingelhoeffer[9] of the rate of reaction (2). By passing atomic chlorine into hydrogen they determined the probability of a chlorine atom's reacting, using the formula
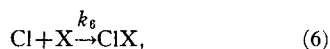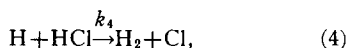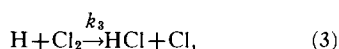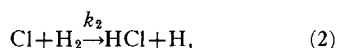
$$W = \frac{\text{HCl formed}}{\text{Cl introduced}}/2Z',$$

where Z' is the number of collisions between Cl and H_2 calculated from kinetic theory, and W is the probability of reaction at each collision. Rodebush and Klingelhoeffer have calculated A_2 from the temperature coefficient of W. We have also calculated A_2 directly from the formula

$$W = e^{-A_2/RT}.$$

The results by these two methods accord very well and give for $A_2(\text{Cl}+H_2)$ a value of 6 Kg.Cals.

The problem may also be indirectly approached through a consideration of the photochemical reaction in the absence of oxygen. Bodenstein and Unger,[8] using the following set of reactions taken from the larger number presented before:

$$\text{Cl}_2 + h\nu \xrightarrow{k_1} 2\text{Cl}. \tag{1}$$

$$\text{Cl} + H_2 \xrightarrow{k_2} \text{HCl} + H, \tag{2}$$

$$H + \text{Cl}_2 \xrightarrow{k_3} \text{HCl} + \text{Cl}, \tag{3}$$

$$H + \text{HCl} \xrightarrow{k_4} H_2 + \text{Cl}, \tag{4}$$

$$\text{Cl} + X \xrightarrow{k_6} \text{ClX}, \tag{6}$$

$$H + X \xrightarrow{k_7} HX, \tag{7}$$

developed this theoretical expression:

$$\frac{d[\text{HCl}]}{dt} = \frac{4k_2 k_3 \cdot I_{abs.} [H_2] \cdot [\text{Cl}_2]}{k_2 k_7 [H_2] + k_3 k_6 [\text{Cl}_2] + k_4 k_6 [\text{HCl}]}.$$

On the other hand they found experimentally,

$$d[\text{HCl}]/dt = k I_{abs.} [H_2].$$

[9] Rodebush and Klingelhoeffer, J. Am. Chem. Soc. 55, 130 (1933).

This empirical equation has recently been checked by Potts and Rollefson.[10] It could only be accounted for if reactions (4) and (7) were very slow compared to (3) and (6), respectively. When only reactions (1), (2), (3) and (6) are considered, the theoretical expression found is
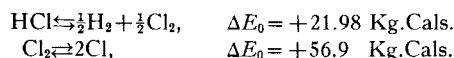
$$d[\text{HCl}]/dt = (2k_2/k_6)[H_2]/[X] I_{abs.},$$

which agrees with the theoretical equation if $[X]$ be constant. If we assume that all of the terms in this expression are practically independent of temperature except k_2/k_6, the temperature coefficient will depend on k_2/k_6 and gives the difference in activation energy between reactions (2) and (6).

Hertel[11] found the temperature coefficient in the absence of oxygen to be 1.37 between 25 and 35°. This calculates to a difference in activation energies of 5.9 Kg.Cals. Potts and Rollefson[10] by the same method find the difference to be 5.8 Kg.Cals. These values agree well with the absolute value found by Rodebush and Klingelhoeffer for reaction (2) alone, indicating that $(\text{Cl}+X)$ requires no activation. In any case this result is a minimum activation energy for reaction (2). We, therefore, write

$$A_2(\text{Cl}+H_2) = 6.0 \text{ Kg.Cals.}$$

The activation for the reverse reaction may be obtained from a coupling of the above result with thermal data. Best present day values as compiled by B. Lewis and von Elbe[12] give

$$\text{HCl} \rightleftharpoons \tfrac{1}{2}H_2 + \tfrac{1}{2}\text{Cl}_2, \quad \Delta E_0 = +21.98 \text{ Kg.Cals.}$$
$$\text{Cl}_2 \rightleftharpoons 2\text{Cl}, \quad \Delta E_0 = +56.9 \text{ Kg.Cals.}$$

A proper combination of these with the value given before for hydrogen dissociation yields

$$\text{Cl} + H_2 \rightarrow \text{HCl} + H, \quad \Delta E_0 = 1.0 \text{ Kg.Cals.}$$

By subtracting this from $A_2(\text{Cl}+H_2)$ one obtains the activation energy of the reverse reaction, $A_4(H+\text{HCl}) = 5$ Kg.Cals.

The evaluation of the energy of activation for reaction (3) is less certain. The reaction occurs

[10] Potts and Rollefson, J. Am. Chem. Soc. 57, 1027 (1935).
[11] Hertel, Zeits. f. physik. Chemie B15, 325 (1931).
[12] B. Lewis and von Elbe, J. Am. Chem. Soc. 57, 612 (1935).

rapidly at room temperatures[13, 14] but the measurements are not of such a type that activation energies may be calculated from them. The matter must be attacked indirectly through a consideration of experiments on the photochemical combination in the presence of oxygen, along with some other data.

In the presence of oxygen reactions (1), (2) and (3) start and continue the chain. Reaction (4) may be omitted since it was shown that it is negligible compared to (3). The chain-ending mechanism is believed to be

$$H + O_2 + M \xrightarrow{k_9} HO_2 + M, \qquad (9)$$
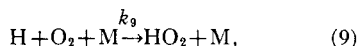
where M is a third body. The reasons for this belief will be brought out later. These reactions lead to the following kinetic equation:

$$\frac{d[HCl]}{dt} = k_1[Cl_2] + \frac{2k_1k_3}{k_9} \frac{[Cl_2]^2}{[M][O_2]}. \qquad (a)$$

Since with moderate oxygen content the chain length is still of the order of 100 and $k_1[Cl_2]$ involves only the first step, the equation may be approximated to

$$\frac{d[HCl]}{dt} = \frac{2k_1k_3}{k_9} \frac{[Cl_2]^2}{[M][O_2]}. \qquad (b)$$

The temperature coefficient of the rate in this case depends chiefly on k_3/k_9. Values of the temperature coefficient per 10°, found by various authors at room temperature are: 1.12 by Hertel,[11] 1.19 by Padoa,[15] 1.10 by Porter, Bardwell and Lind.[16] The activation energy calculated from these values will represent $(A_3 - A_9)$. Evaluation gives for $(A_3 - A_9)$ 2.1, 2.9 and 1.8 Kg.Cals., respectively.

Krauskopf and Rollefson[17] found $(A_3 - A_9)$ in a different way. The partition of the hydrogen reacting in a system containing oxygen and chlorine between H_2O and HCl was directly

determined. Applications of equation (a) above and the equation

$$d[H_2O]/dt = k_1[Cl_2],$$

assuming one molecule of water formed for each hydrogen atom reacting with oxygen leads to

$$\frac{H_2 \text{ used in } H_2O}{\text{total } H_2 \text{ reacting}} = U$$

$$= \frac{2}{3 + 2k_3/k_9 \cdot [Cl_2]/[O_2][M]}.$$

From the observation that when $[O_2]/[Cl_2]$ is 20, $U = 0.57$ at 0° and 0.40 at 85°C, they calculate the difference $(A_3 - A_9)$ to be 1.6 Kg.Cals.

All these values represent a minimum for the activation energy A_3, since A_9 is not likely to be negative. This gives $A_3(H + Cl_2)$ is greater than 2 Kg.Cals.

The upper limit may also be determined. Bodenstein and Unger[8] concluded from their data that HCl did not inhibit the reaction in the absence of oxygen, and that consequently reaction (4) was slow compared to reaction (3). This is confirmed by the work of Potts and Rollefson.[10] Let us therefore make the assumption that

$$k_3/k_4 > 100.$$

Since we wish to make sure of having a maximum value for A_3, an "orientation factor" of 1/10 will be allowed for $H + HCl$ as was indicated for $H + HBr$. Then

$$k_3/k_4 = (Z_{12}^{-A_3/RT}/0.1 Z_{12}^{-A_4/RT}) > 100.$$

From this is obtained $A_4 - A_3 > 1.4$ Kg.Cals. Since A_4 has already been determined to be 5 Kg.Cals., this gives $A_3 < 3.6$ Kg.Cals.

Another method for obtaining a maximum value follows. Bonhoeffer and a co-worker[18] tried to measure the para- to ortho-hydrogen conversion in a mixture of para-hydrogen and chlorine when illuminated. Their method was accurate enough to determine one percent of para- to ortho-conversion, but they were unable to detect any change. This means that
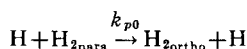
[13] Boehm and Bonhoeffer, Zeits. f. physik. Chemie 119, 385 (1926).
[14] Marshall, J. Phys. Chem. 29, 842 (1925).
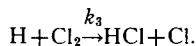[15] Padoa and Buttironi, Atti. Linc. 25, 215 (1916); Gazz. 47, 6 (1917).
[16] Porter, Bardwell and Lind, J. Am. Chem. Soc. 48, 2603 (1926).
[17] Krauskopf and Rollefson, J. Am. Chem. Soc. 56, 325 (1934).

[18] Geib and Hartek, Zeits. f. physik. Chemie B15, 116 (1932).

$$H + H_{2_{para}} \xrightarrow{k_{p0}} H_{2_{ortho}} + H$$

is slow compared with

$$H + Cl_2 \xrightarrow{k_3} HCl + Cl.$$

The assumption may be made then that

$$k_{p0}/k_3 < 0.01.$$

Then we have

$$k_{p0}/k_3 = (Z_{12}^{-A_{p0}/RT}/Z_{12}^{-A_3/RT}) < 0.01.$$

Taking the Z_{12} factors in this case to be the same, we have

$$e^{-A_{p0}/RT}/e^{-A_3/RT} < 0.01$$

or $A_{p0} - A_? < 2.8$ Kg.Cals. Since A_{p0} has been determined to be in the neighborhood of 7.0 Kg.Cals.[19] a maximum value for A_3 of 4.2 Kg.Cals. is obtained.

Since a minimum value for A_3 of 1.6 to 2.9 Kg.Cals. has been obtained and a maximum value of 3.6 to 4.2 Kg.Cals., a value, $A_3(H + Cl_2) = 2$–3 Kg.Cals., is indicated.

It is now necessary to return to a consideration of the chain-ending mechanism in the presence of oxygen, for which

$$H + M + O_2 \rightarrow HO_2 + M \qquad (9)$$
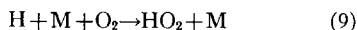
has been used. Various experiments have quite definitely established that the chain-ending mechanism must involve a reaction of hydrogen atoms with oxygen rather than chlorine atoms with oxygen. Thus, Schwab and Friess[20] passed atomic chlorine into oxygen and found no measurable reaction whatever. Further, the logical product of a reaction of chlorine atoms with oxygen, ClO_2, is known to be a very strong inhibitor for the reaction,[21] so that if this product were formed, the rate would decrease rapidly. No such result has ever been observed. Thirdly, a study of yields of H_2O and HCl in very high oxygen-containing mixtures led Krauskopf and Rollefson[17] to the conclusion that $(Cl + O_2)$ could play only a very small part, if any, in stopping

the chains. Lastly the types of kinetic expressions obtained experimentally indicate that oxygen breaks the chains by reaction with hydrogen atoms.

Bodenstein and Schenck[22] first showed that the reaction of hydrogen atoms with oxygen was logically a three-body process. They observed that although the activation energy of the atomic H and O_2 reaction was 2 Kg.Cals. less than that of H and Cl_2 and consequently should proceed 50 times as fast as the latter, nevertheless comparative yields of HCl and H_2O in $H_2 - O_2 - Cl_2$ mixtures containing equal amounts of Cl_2 and O_2 showed the rate of $H + Cl_2$ to be twenty times faster than $H + O_2$. This meant that only 1 in 1000 (20 times 50) of the bimolecular collisions with sufficient activation energy between hydrogen and oxygen was effective. Since 1 : 1000 is approximately the ratio of trimolecular to bimolecular collisions, it appeared that $H + O_2$ must involve a third body.

This position has received confirmation from Bates[23] who shows quite conclusively that the chain-ending reaction is a three-body process. Cook and Bates[23] studied the inhibition of the photodecomposition of HI in presence of oxygen, which involves $(H + O_2)$. Considering the reactions

$$H + HI \xrightarrow{k_\alpha} H_2 + I, \qquad (\alpha)$$

$$H + O_2 \xrightarrow{k_\beta} HO_2 \qquad (\beta)$$
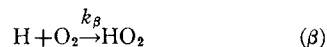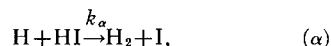
they found that using a bimolecular reaction for (β), k_α/k_β was about 10 at 100 mm HI and 100 mm O_2, but decreased to 3 when 300–400 mm of N_2 was added. If a trimolecular reaction were employed,

$$H + M + O_2 \xrightarrow{k_\beta'} HO_2 + M \qquad (\beta')$$
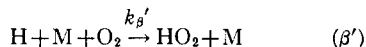
then the ratio k_α/k_β' remained constant throughout. Thus the chain-ending mechanism seems quite definitely to be a three-body process.

The theory on which the values in this reaction chain are based is that developed by Bodenstein and various co-workers. Some recent

[19] Geib and Hartek, Zeits. f. physik. Chemie, Bodensteinband 849 (1931).
[20] Schwab and Friess, Zeits. f. Electrochim. 39, 586 (1933).
[21] Chapman and MacMahon, J. Chem. Soc. 97, 845 (1909).

[22] Bodenstein and Schenck, Zeits. f. physik. Chemie B20, 420 (1933).
[23] Bates and Lavin, J. Am. Chem. Soc. 55, 81 (1933); Cook and Bates, J. Am. Chem. Soc. 57, 1775 (1935).

researches, notably the extensive ones of Norrish and Ritchie,[24] are at variance with this scheme. Thus, while Bodenstein had found a variation of the rate of reaction in oxygen-free mixtures depending on the first power of the light absorbed, Norrish and Ritchie found a dependence on the 0.6 power. This is explained on the basis that the chain-ending mechanism is a recombination of chlorine atoms, rather than a reaction of the type

$$Cl + X \rightarrow ClX.$$
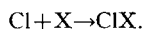
Thus, either chain-breaking mechanism may be correct, depending on the experimental conditions. This is confirmed by Potts and Rollefson,[10] who found a first power dependence at room temperature and a 0.5 power dependence at liquid-air temperatures. Since $Cl + H_2$ occurs 1 in 10^5 collisions at room temperature and only 1 in 10^8 at liquid-air temperatures, $[Cl]$ will be enormously increased and thus

$$Cl + Cl + M \rightarrow Cl_2 + M$$

the rate of which depends on the square of the chlorine concentration, will be greatly favored at liquid-air temperatures as compared to

$$Cl + X \rightarrow ClX$$
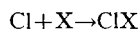
the rate of which depends only on the first power of the chlorine concentration. However, either chain-breaking mechanism leads to the same type of variation with temperature and allows the same conclusions to be drawn concerning the activation energy of $(Cl + H_2)$. The Bodenstein mechanism has been used because Hertel,[11] and Potts and Rollefson,[10] whose values for the temperature coefficient were used, both found a first-power dependence on light absorbed.

A second difference is more serious. Bodenstein and Unger[8] found no inhibition by HCl in the absence of oxygen, and Bodenstein and Schenck[22] found none in the presence of oxygen. Norrish and Ritchie[24] find serious retardation by that substance in both cases. They ascribe this to the reaction $H + HCl \rightarrow H_2 + Cl$ which they consider to be comparable in rate to $H + Cl_2 \rightarrow HCl + Cl$. This is not only opposed to Bodenstein's mechanism, but also is inconsistent with their own

results. For, from thermodynamic considerations $(Cl + H_2)$ and $(H + HCl)$ must have approximately similar rates[10] $(\Delta E_0 = 1.0$ cals.$)$. On Norrish and Ritchie's assumptions, therefore

$$Cl + H_2 \xrightarrow{k_2} HCl + H \quad \text{and} \quad H + Cl_2 \xrightarrow{k_3} HCl + Cl$$
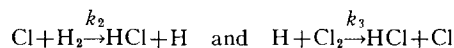
have rate constants of the same order of magnitude. Thus, in an equimolecular reaction system, since these two reactions must be proceeding at the same rate in order to maintain steady state atomic concentrations

$$k_2[Cl][H_2] \cong k_3[H][Cl_2],$$

whence $[Cl] \cong [H].$

If this be true, then $Cl + Cl + M \rightarrow Cl_2 + M$, $H + Cl + M \rightarrow HCl + M$, and $H + H + M \rightarrow H_2 + M$ should all be effective in breaking chains. Yet neither of the latter two reactions enter into Norrish and Ritchie's kinetic expression and they state that a mechanism which considers these as chain-breaking reactions does not fit the experimental facts. Either both

$$H + HCl \rightarrow H_2 + Cl$$

and
$$\left\{ \begin{array}{l} H + H + M \rightarrow H_2 + M \\ H + Cl + M \rightarrow HCl + M \end{array} \right\}$$
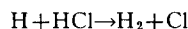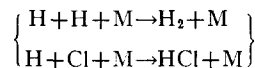
must enter the kinetic expression or neither can enter. The evidence indicates the latter.

So, although Norrish and Ritchie have undoubtedly obtained excellent experimental results, their explanation of them does not hold. On the other hand, their results in the presence of oxygen are easily explained by adopting the three-body process $(H + M + O_2)$ as the chain-breaking mechanism, where HCl is an effective third body. Their results in the absence of oxygen are only partly explained by the trimolecular recombination of chlorine atoms. However, some light has recently been thrown on this point by the experiments of Rodebush and Spealman,[25] which seem to indicate that $H + HCl$ may occur rapidly as a catalytic reaction on the surface of Pyrex. If the walls of Norrish and Ritchie's vessels were active in this way, their results are easily accounted for. In view of these facts the

[24] Norrish and Ritchie, Proc. Roy. Soc. **A140**, 112, 713 (1933).

[25] Rodebush and Spealman, J. Am. Chem. Soc. **57**, 1040 (1935).

Bodenstein mechanism seems to be the correct one to use to obtain the rates of the homogeneous reactions.

HYDROGEN-IODINE REACTION

Work on the atomic reactions in this case is quite scanty since the ordinary combination is a molecular process. However, there is sufficient evidence to obtain approximate values.

From his studies of the photodecomposition of hydrogen iodide in presence of oxygen, Bates[23] concludes that for the reactions

$$H+HI \xrightarrow{k_1} H_2+I, \qquad (1)$$

$$H+O_2+M \xrightarrow{k_9} HO_2+M, \qquad (9)$$
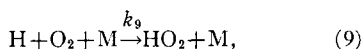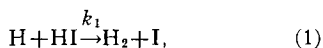
k_1 is about ten times k_9 when k_9 is regarded as a bimolecular constant. Later work indicated that reaction (9) is in fact trimolecular, as it is written above. Since the ratio of bimolecular to trimolecular collisions is of the order of 1000, k_1 would be 1000 times k_9 if every collision were effective in both reactions. Allowing an orientation factor of 10 for reaction (1), as was found for the analogous reaction $H+HBr \rightarrow H_2+Br$, this is reduced to a factor of 100, which is to be compared to the observed ratio of 10. One concludes that reaction (1) may require an activation energy, $A_1(H+HI) \sim 1$ Kg.Cal.

The value for the reverse of this reaction may be found from thermal data. Beutler's[4] value for hydrogen was

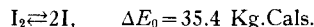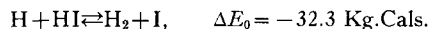$$H_2 \rightleftarrows 2H, \qquad \Delta E_0 = 102.68 \text{ Kg.Cals.}$$
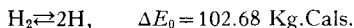
Landolt-Börnstein[26] give

$$H_2+I_2 \rightleftarrows 2HI, \qquad \Delta E_0 = -2.8 \text{ Kg.Cals.}$$

The value for the dissociation of iodine is taken

from Brown[27]

$$I_2 \rightleftarrows 2I, \qquad \Delta E_0 = 35.4 \text{ Kg.Cals.}$$

These lead to a value

$$H+HI \rightleftarrows H_2+I, \qquad \Delta E_0 = -32.3 \text{ Kg.Cals.}$$
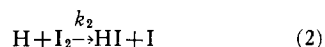
The activation energy of the reverse reaction is obtained by addition and gives $A_3(I+H_2) = 33$ Kg.Cals.

From the observation of Farkas and Bonhoeffer[28] that 15 percent of iodine completely inhibits the photodecomposition of HI they conclude that

$$H+I_2 \xrightarrow{k_2} HI+I \qquad (2)$$

occurs 100 times as frequently as reaction (1) or therefore at practically every collision. This means that $A_4(H+I_2) \sim 0$.

COMPARISON OF VALUES

A comparison of the results obtained by this study with those obtained by theoretical calculation[29] by Eyring's method by using a 14 percent Coulombic term is shown in Table I. The

TABLE I.

	$H+Cl_2$	$H+Br_2$	$H+I_2$	$H+HCl$	$H+HBr$	$H+HI$	$Cl+H_2$	$Br+H_2$	$I+H_2$
Experimental	3	1.0	0	5	1	1	6.0	17.7	33
Eyring	2.4	2.2	1.4	11.8	6.6	7.6	12.8	24.0	40

results agree quite well as to order, but the calculated values tend to run higher. It may be noted that a larger Coulombic term would lead to better agreement in the majority of cases.

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[26] Landolt-Börnstein, *Tabellen*, Erster Erganzungsband, p. 809.

[27] Brown, Phys. Rev. **38**, 709 (1931).
[28] Farkas and Bonhoeffer, Zeits. f. physik. Chemie **132**, 235 (1928).
[29] Private communication, H. Eyring and A Wheeler.