The Radiochemical Synthesis and Decomposition of Hydrogen Bromide

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A theory is developed for the radiochemical synthesis and decomposition of hydrogen bromide which makes use of experimentally known processes of ionization, the known rates of a few simple chemical reactions, and the extensive experimental results of Lind and Livingston. The analysis indicates that in pure hydrogen gas, six hydrogen atoms are formed per ion pair; in pure hydrogen bromide, six hydrogen bromide molecules would be decomposed; and in equal mixtures of Br_2 and HBr the chance that an electron will form negative ions with HBr (HBr $+\epsilon \rightarrow H + Br^-$) is greater than with Br_2.

IN most radiochemical experiments, the number of molecules reacting for each ion pair formed is largely independent of the stoichiometrical composition of the mixture of gases. However, the recent very careful investigations of Lind and Livingston[1] show that the synthesis and decomposition of hydrogen bromide vary greatly with the relative pressures of the hydrogen, bromine and hydrogen bromide. In this paper, we develop an explanation for the observed yields which is based upon a knowledge of the processes of ionization in these gases and the rates of a few simple chemical reactions.

1. *The Primary Ionization Processes.*—The ionization processes in pure hydrogen have been considered in a previous paper.[2] The alpha-particle ionizes the hydrogen to form H_2^+.

$$H_2 + \alpha \rightarrow H_2^+ + \epsilon + \alpha. \qquad (1)$$
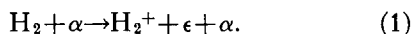
The formation of H^+ is less frequent. There is considerable evidence that the alpha-particle gives up part of its energy by exciting the molecules without ionizing them.

$$H_2 + \alpha \rightarrow H_2' + \alpha. \qquad (2)$$
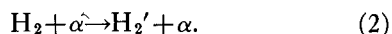
These energy rich molecules may subsequently dissociate to form two hydrogen atoms. The energy of the alpha-particle consumed is equivalent to 33 ev per pair of ions produced. Since the ionization process requires 15.4 ev per ion pair as minimum ionization energy it is evident that quantities of energy roughly equivalent to those consumed in ionization may be used for molecular excitation.

Blewett[3] has recently studied in the mass spectrograph the ionization processes in bromine for slow electron collisions. He finds that Br_2^+ and Br^+ are formed. For the high speed collisions between alpha-particles and bromine molecules it is impossible at present to say on the basis of experiments alone which ionization would occur most frequently. Also, bromine atoms will be formed by the intermediate production of excited bromine molecules. However, it is quite immaterial for the purposes of this paper to consider these species since we shall find that the bromine atoms as well as the bromine positive ions cannot essentially affect either the synthesis or the dissociation of hydrogen bromide.

Little work has been done with the mass spectrograph on the ionization processes in hydrogen bromide. However, Blewett obtained HBr^+ from impurities in his bromine gas and this is undoubtedly the principal ion which is first formed in the hydrogen bromide. Just as in the case of hydrogen and of bromine, we should also expect the formation of excited molecules which subsequently dissociate to form the separate atoms.

$$HBr + \alpha \rightarrow HBr' \rightarrow H + Br. \qquad (3)$$
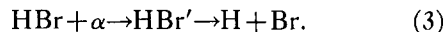
The yield of $H_2 + Br_2$ from HBr per ion pair, which Lind and Livingston measured, provide excellent data for determining the frequency with which reactions of type (3) occur.

2. *Secondary Ionization Processes in the Individual Gases.*—There is considerable evidence that the reaction:

$$H_2^+ + H_2 \rightarrow H_3^+ + H \qquad (4)$$
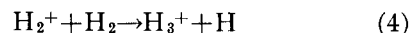
[1] Lind and Livingston, J. Am. Chem. Soc. **58**, 612 (1936).
[2] Eyring, Hirschfelder and Taylor, J. Chem. Phys. **4**, 479 (1936).
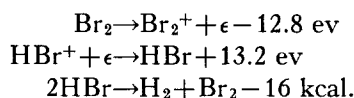[3] Blewett, Phys. Rev. **49**, 900 (1936); Blewett, Ph.D. dissertation, Princeton, 1936.

takes place with great frequency.[2] The corresponding reactions for bromine ions:

$$Br_2^+ + Br_2 \rightarrow Br_3^+ + Br$$
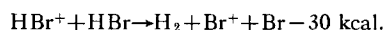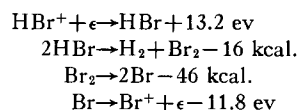$$Br^+ + Br_2 \rightarrow Br_3^+ \qquad (5)$$
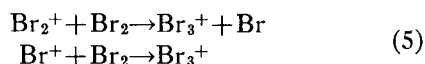
have not been investigated, but their occurrence is immaterial from the standpoint of this paper. With hydrogen bromide this type of reaction is of considerable interest:

$$HBr^+ + HBr \rightarrow H_2 + Br_2^+ \qquad (6a)$$
$$\rightarrow H_2Br^+ + Br. \qquad (6b)$$
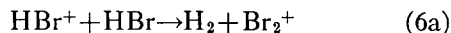
Reaction (6a) requires an energy of 7 kcal. if we consider the following thermal data:

$$Br_2 \rightarrow Br_2^+ + \epsilon - 12.8 \text{ ev}$$
$$HBr^+ + \epsilon \rightarrow HBr + 13.2 \text{ ev}$$
$$2HBr \rightarrow H_2 + Br_2 - 16 \text{ kcal.}$$

This value for the necessary energy is within the estimated limits of error of the ionization potentials of HBr and of Br_2, i.e., 0.5 ev, and might therefore be spurious. Blewett has observed the presence of H_2Br^+ ions, and reaction (6b) can occur if the binding of H_2 to Br^+ exceeds 30 kcal. since:

$$HBr^+ + \epsilon \rightarrow HBr + 13.2 \text{ ev}$$
$$2HBr \rightarrow H_2 + Br_2 - 16 \text{ kcal.}$$
$$Br_2 \rightarrow 2Br - 46 \text{ kcal.}$$
$$Br \rightarrow Br^+ + \epsilon - 11.8 \text{ ev}$$

$$\overline{HBr^+ + HBr \rightarrow H_2 + Br^+ + Br - 30 \text{ kcal.}}$$

This required binding energy of Br^+ with H_2 of more than 30 kcal. does not seem excessive since we know that Br^+ binds H to form HBr^+ with 50 kcal. and also that H^+ binds H_2 with more than 50 and probably 70 kcal. Lacking further information we shall, therefore, consider reaction (6b) as occurring frequently and rule out reaction (6a) from energy considerations.

The fate of electrons in H_2, Br_2, and HBr is well known. The electron affinity of H is so small and the activation energy required for its formation so great that
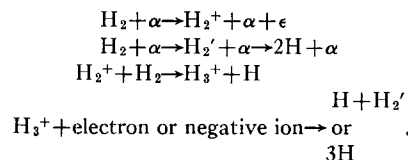
$$H_2 + \epsilon \rightarrow H + H^-$$
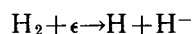
is indeed a rare process. However, bromine has such a large electron affinity,[3, 4] i.e., 88 kcal., that slow electrons are rapidly absorbed in HBr

and Br_2 to form Br^- ions. Some Br_2^- ions are also formed. It is interesting to note that Blewett was unable to detect any HBr^- ions. In the interpretation of the synthesis and decomposition of hydrogen bromide we will have to consider the relative rate of reaction of an electron with HBr and with Br_2. The negative ions formed neutralize the positive ions liberating free atoms, etc. As we shall show later, our conclusions from the Lind and Livingston experiments indicate that an electron in a mixture of equal amounts of HBr and Br_2 reacts more often with HBr than with Br_2.
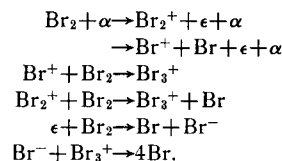
Combining the various processes, we obtain for the mechanisms in the pure gases:

(a) Hydrogen:

$$H_2 + \alpha \rightarrow H_2^+ + \alpha + \epsilon$$
$$H_2 + \alpha \rightarrow H_2' + \alpha \rightarrow 2H + \alpha$$
$$H_2^+ + H_2 \rightarrow H_3^+ + H$$
$$H_3^+ + \text{electron or negative ion} \rightarrow \begin{array}{l} H + H_2' \\ \text{or} \\ 3H \end{array}.$$

The yield of H atoms per ion pair is therefore approximately 4 for those molecules which are dissociated by the ionic mechanism. To these must be added whatever H atoms are produced by dissociation without ionization. Our interpretation of the Lind and Livingston experiments indicate that 2 H atoms are produced per ion pair in this latter fashion. This yield is in agreement with our interpretation of the *ortho-para* hydrogen conversion which was studied by Capron.[5]

(b) Bromine: For our purposes the yield of Br atoms from Br_2 molecules is quite immaterial. The principal reactions probably are:

$$Br_2 + \alpha \rightarrow Br_2^+ + \epsilon + \alpha$$
$$\rightarrow Br^+ + Br + \epsilon + \alpha$$
$$Br^+ + Br_2 \rightarrow Br_3^+$$
$$Br_2^+ + Br_2 \rightarrow Br_3^+ + Br$$
$$\epsilon + Br_2 \rightarrow Br + Br^-$$
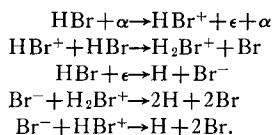$$Br^- + Br_3^+ \rightarrow 4Br.$$

This would indicate that around 6 Br atoms are formed in the ionic processes per ion pair and to this must be added the number which are formed by dissociation of Br_2 without ionization.
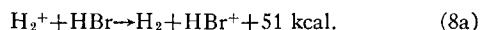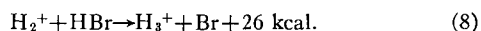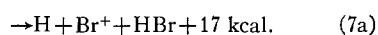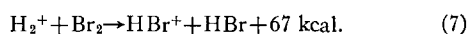
(c) Hydrogen Bromide:

[4] Glockler, A. C. S. Meeting, Kansas City, 1936

[5] Capron, Ann. soc. sci. Bruxelles **B55**, 222–36 (1935).

$$HBr + \alpha \rightarrow HBr^+ + \epsilon + \alpha$$
$$HBr^+ + HBr \rightarrow H_2Br^+ + Br$$
$$HBr + \epsilon \rightarrow H + Br^-$$
$$Br^- + H_2Br^+ \rightarrow 2H + 2Br$$
$$Br^- + HBr^+ \rightarrow H + 2Br.$$

Thus, between two and three H atoms are produced per ion pair through the ionic mechanisms.

3. *Secondary Ionization Processes in Mixed Gases.*—In addition to the ionic mechanisms which we have just considered, we must also examine the possibility of reactions in which the initial ionization in one gas produces effects in molecules of another species. H_2^+ can participate in two reactions of this nature.

$$H_2^+ + Br_2 \rightarrow HBr^+ + HBr + 67 \text{ kcal.} \tag{7}$$
$$\rightarrow H + Br^+ + HBr + 17 \text{ kcal.} \tag{7a}$$
$$H_2^+ + HBr \rightarrow H_3^+ + Br + 26 \text{ kcal.} \tag{8}$$
$$H_2^+ + HBr \rightarrow H_2 + HBr^+ + 51 \text{ kcal.} \tag{8a}$$

Reactions (7) and (7a) cut down by one the yield of hydrogen bromide molecules in the synthesis since they are in competition with the reaction $H_2^+ + H_2 \rightarrow H_3^+ + H$. The fact that we do not need to consider any such inhibitory property of Br_2 in our subsequent explanation of the synthesis indicates that (7) is not important, and suggests that the reaction may have a considerable activation energy. Reaction (8) may or may not occur but it does not affect the yield. Reaction (8a) would cut down the yield of H atoms and total yields in both synthesis and decomposition of hydrogen bromide.

Bromine ions could participate in the following:

$$Br_2^+ + H_2 \rightarrow HBr^+ + HBr + 7 \text{ kcal.} \tag{9}$$
$$\rightarrow H_2Br^+ + Br$$
$$Br^+ + H_2 \rightarrow H_2Br^+. \tag{10}$$
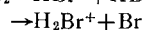
These would indicate that bromine should increase the yield over the values which we would expect from neglecting them. Either reaction (7) and either (9) or (10) occur and nicely counterbalance one another or else none of them occur with any frequency for the data on the synthesis of hydrogen bromide can be well explained for all ratios of H_2 to Br_2 neglecting such processes. It is interesting to note that the reactions:

$$Br_2^+ + HBr \rightarrow Br_2 + HBr^+ - 9 \text{ kcal.} \tag{11}$$
$$Br^+ + HBr \rightarrow Br + HBr^+ - 32 \text{ kcal.} \tag{12}$$

are energetically improbable.

The HBr ions might react in the following manner:

$$HBr^+ + Br_2 \rightarrow Br_2^+ + HBr + 9 \text{ kcal.} \tag{13}$$
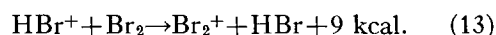
Reaction (13) certainly is not important since we find a somewhat larger yield for the decomposition of HBr in the presence of Br_2 than we expect. The reaction

$$HBr^+ + H_2 \rightarrow H_3^+ + Br - 25 \text{ kcal.} \tag{14}$$

is energetically improbable.

We may now analyze the data of Lind and Livingston first neglecting the effects of these ionic reactions between different species and then examining how far effects of these various types may influence the calculated yields.

4. *Synthesis and Decomposition of Hydrogen Bromide.*—In a mixture of hydrogen bromide, bromine and hydrogen the number of ion pairs found initially depends on the partial pressures, stopping powers, and specific ionizations of the gases present. The ratio of the number of positive ions of a species to the total number obeys a simple law of mixing:[6]

$$\frac{N_{H_2}}{N} = \frac{S_{H_2}I_{H_2}P_{H_2}}{S_{H_2}I_{H_2}P_{H_2} + S_{Br_2}I_{Br_2}P_{Br_2} + S_{HBr}I_{HBr}P_{HBr}},$$
$$\frac{N_{HBr}}{N} = \frac{S_{HBr}I_{HBr}P_{HBr}}{S_{HBr}I_{HBr}P_{HBr} + S_{H_2}I_{H_2}P_{H_2} + S_{Br_2}I_{Br_2}P_{Br_2}},$$
$$N = N_{HBr} + N_{H_2} + N_{Br_2}.$$

Here N with the appropriate subscript represents the number of ion pairs formed in the indicated gas. N without the subscript is the total number of ion pairs. The S's are the specific stopping powers of the gases and the I's are the specific numbers of ion pairs formed in the pure gases with respect to air $= 1$. The P's are the partial pressures of the gases and we shall express them in millimeters of mercury. The values of the stopping powers are well known and they should be quite accurate:[6]

$$S_{H_2} = 0.24 \quad S_{Br_2} = 2.80 \quad S_{HBr} = \tfrac{1}{2}(S_{H_2} + S_{Br_2}) = 1.52.$$

The values for the specific number of ion pairs are much more difficult to measure. The values which we use are:

$$I_{H_2} = 1.0 \text{ (reference 6)} \quad I_{Br_2} = 1.35 \text{ (reference 6)}$$
$$I_{HBr} = 1.29 \text{ (reference 7)}$$

[6] Glockler and Livingston, J. Phys. Chem. **38**, 655 (1934).
[7] Lind, "Chemical Effects of Alpha Particles," Chem. Monograph, p. 36 (1928).

and they may be inaccurate. Any error in these values will make corresponding errors in the following analysis. For example, if I_{HBr} were 1 instead of 1.29 we would find a yield of 5 instead of 6 H atoms per ion pair in nearly pure hydrogen containing small amounts of bromine.

After the ionic reactions have taken place a certain number of H and Br atoms are produced and also a certain number of hydrogen bromide molecules are formed or decomposed according to whether the initial ionization (or dissociation without ionization) has taken place in hydrogen, bromine or hydrogen bromide. The chemical reactions which these atoms may undergo have been carefully studied by Bodenstein, Lind, Jung, Bonhoeffer, and others.[8] Hydrogen atoms may react with either hydrogen bromide or with bromine:

$$H + Br_2 \xrightarrow{k_3} HBr + Br + 36 \text{ kcal.}$$

$$H + HBr \xrightarrow{k_4} H_2 + Br + 16.7 \text{ kcal.}$$
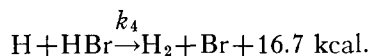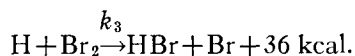
In fact Bodenstein and Jung[9] have obtained an accurate value for the ratio

$$k_3/k_4 = 8.4.$$

Using this ratio, if B is the chance that an H atom will react with Br_2 to form HBr rather than reacting with HBr to destroy an HBr, then

$$B = \frac{k_3(H)(Br_2)}{k_4(H)(HBr) + k_3(H)(Br_2)}$$
$$= \frac{1}{1 + (1/8.4)(P_{HBr}/P_{Br_2})}.$$

The reactions of Br with HBr and with H_2 require too large an amount of energy to take place to any appreciable extent.

$$Br + HBr \rightarrow Br_2 + H - 36 \text{ kcal.} \qquad (15)$$

$$Br + H_2 \rightarrow HBr + H - 16.7 \text{ kcal.} \qquad (16)$$
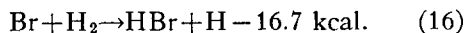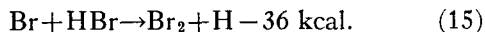
Before setting up an expression for the yield we must consider the probability that an electron will react with HBr to form Br^- rather than with Br_2 to form this same negative ion.

$$\epsilon + Br_2 \xrightarrow{k_1} Br^- + Br \qquad (17)$$
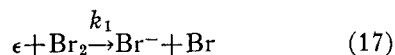
[8] Morris and Pease, J. Chem. Phys. **3**, 796 (1935).
[9] Bodenstein and Jung, Zeits. f. physik. Chemie **121**, 127 (1926).

$$\epsilon + HBr \xrightarrow{k_2} Br^- + H \qquad (18)$$
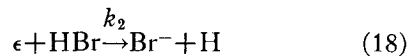
We define the probability A of (18) occurring rather than (17) by:

$$A = \frac{k_2(HBr)}{k_1(Br_2) + k_2(HBr)} = \frac{1}{1 + (k_1/k_2)(P_{Br_2}/P_{HBr})}.$$

The ratio of k_1/k_2 is not known experimentally but our interpretation of the Lind and Livingston data indicate that k_2 is considerably larger than k_1. The fact that the heat of dissociation of HBr, i.e., 82 kcal. is so close to the electron affinity of Br, 88 kcal., makes this seem plausible.

In the mixture of hydrogen, hydrogen bromide and bromine when the initial energy is taken up from the alpha-particle by hydrogen, let "a" H atoms be produced by going through positive ion reactions and subsequent neutralization and by dissociation without ionization. When this initial energy is taken up by hydrogen bromide, let "b" atoms of H be produced and "b" atoms of hydrogen bromide be thereby decomposed. The bromine, of course, produces no such effect owing to the nonreactivity of bromine with either hydrogen or hydrogen bromide. In each of these types of initial ionization, one electron is produced and is absorbed rapidly by either bromine or hydrogen bromide. This electron has the chance A that it will react with hydrogen bromide to produce an additional H atom and thereby decompose one more hydrogen bromide than if the electron were captured by bromine. Thus, altogether, the number of H atoms produced is:

$$aN_{H_2} + bN_{HBr} + AN.$$

The number of HBr molecules decomposed directly is:

$$bN_{HBr} + AN.$$

Remembering that each H atom has the chance B to react with Br_2 to form an HBr and a chance $(1-B)$ to decompose an HBr, we obtain for the yield of HBr per ion pair:

$$\frac{M}{N} = [B - (1-B)]\left[a\frac{N_{H_2}}{N} + b\frac{N_{HBr}}{N} + A\right] - b\frac{N_{HBr}}{N} - A$$
$$= a(2B-1)\frac{N_{H_2}}{N} - 2b(1-B)\frac{N_{HBr}}{N} - 2A(1-B).$$

TABLE I. *Synthesis.*

Time, hrs.	P_{HBr}	P_{Br_2}	P_{H_2}	$(1-B)$	$(2B-1)N_{H_2}/N$	$(1-B)N_{HBr}/N$	$(M/N)_{calc.}$	$(M/N)_{obs.}$
10	3.0	120.5	167.5	.0030	.080	.000	.48	.58
30	8.4	117.8	164.8	.0084	.078	.000	.47	.58
50	12.8	115.6	162.6	.0130	.076	.001	.46	.54
70	16.2	113.9	160.9	.0167	.075	.001	.45	.48
90	18.8	112.6	159.6	.0195	.074	.001	.44	.43
110	21.0	111.5	158.5	.0219	.073	.002	.44	.44
130	23.0	110.5	157.5	.0242	.072	.002	.43	.45
150	24.6	109.7	156.7	.0260	.071	.003	.43	.47

TABLE II. *Decomposition (Assume $A=1$).*

Time, hrs.	P_{HBr}	P_{Br_2}	P_{H_2}	$(1-B)$	$(2B-1)N_{H_2}/N$	$(1-B)N_{HBr}/N$	$(M/N)_{calc.}$	$(M/N)_{obs.}$
10	148.3	10.6	10.6	.625	$-.002$	.545	-3.43	-3.57
30	127.9	20.8	20.8	.423	.002	.317	-2.13	-1.89
50	115.9	26.8	26.8	.340	.006	.231	-1.56	-1.51
70	107.3	31.1	31.1	.291	.009	.183	-1.25	-1.26
90	101.1	34.2	34.2	.260	.012	.154	-1.07	-1.08
110	96.3	36.6	36.6	.239	.014	.134	$-.94$	-1.01
130	92.7	38.4	38.4	.223	.015	.121	$-.84$	$-.88$
150	89.9	39.8	39.8	.212	.016	.111	$-.76$	$-.82$
170	87.7	40.9	40.9	.203	.017	.104	$-.73$	$-.75$

TABLE III. *Summary of experiments.*

Exp.	P_{HBr}	P_{Br_2}	P_{H_2}	$(1-B)$	$(2B-1)N_{H_2}/N$	$(1-B)N_{HBr}/N$	$(M/N)_{calc.}$	$(M/N)_{obs.}$
1	1.2	127.8	84.9	.0011	.040	.000	.24	.24
2	.6	115.4	126.2	.0006	.065	.000	.39	.42
3	3.0	120.5	167.5	.0030	.080	.000	.48	.58
4	2.4	95.5	250.4	.0030	.140	.000	.84	.88
5	5.4	56.6	411.3	.0112	.299	.000	1.79	1.90
6	2.4	58.4	469.3	.0049	.330	.000	1.98	1.76
7	7.8	40.0	456.1	.0227	.379	.001	2.27	2.67
8	3.8	26.4	424.6	.0169	.471	.001	2.83	2.76
9	3.4	29.7	515.1	.0135	.496	.000	2.98	2.85
10	6.4	25.1	502.2	.0295	.498	.002	2.99	2.85
11	4.6	17.9	510.3	.0297	.578	.001	3.47	2.89
12	71.9	136.1	1.0	.0592	.000	.013	$-.17$	$-.89$
13	162.3	4.5	4.5	.811	$-.002$	.768	-4.70	-3.98
14	148.3	10.6	10.6	.625	$-.002$	.545	-3.44	-3.57
15	105.7	5.5	579.5	.696	$-.148$	.393	-3.85	-2.57
16	84.5	1.3	571.1	.885	$-.343$	.477	-5.74	-5.07

Here B, N_{H_2}/N and N_{HBr}/N are known for any experiment. a, b, and a constant in A are not known and must be chosen so as to give the best fit with the experimental data. There are certain limits which we can place on these quantities a priori, i.e., $a>3$, $b>1$, and A lies between 1 and zero. We find the best agreement with experiment by taking

$a=6.0$, $b=2.0$, $A=1$ for large ratios of P_{HBr}/P_{Br_2}.

For smaller ratios the value of A is not important since $(1-B)$ is then small.

Tables I, II and III show the agreement which we obtain with the experiments of Lind and Livingston.[10] We must examine these tables for trends which would indicate the existence of important mixed ionic reactions such as were discussed in a previous section. The agreements in Tables I and II are quite satisfactory and show nothing which could be interpreted as real deviations between the experimental and the

[10] The values for P_{HBr}, P_{H_2}, P_{Br_2} are the partial pressures of the constituents at the end of a 10-hour period of irradiation as calculated from Lind and Livingston's Table III.

calculated values. However, in Table III, experiments 7, 11, 12, 15 and 16 are the least satisfactory. In 7, 11, 15 and 16 we are dealing with a large pressure of hydrogen and an appreciable amount of hydrogen bromide. In the synthesis experiment 11 we calculate too large a yield of hydrogen bromide and in the decomposition experiments we calculate too much decomposition of hydrogen bromide. The reaction which is most plausible to explain these discrepancies is:

$$H_2^+ + HBr \rightarrow H_2 + HBr^+ + 51 \text{ kcal.} \qquad (8a)$$

Experiment 12 is particularly interesting because it is the only experiment in which P_{H_2} is very small and that of Br_2 and HBr are large. For this condition it will be seen that $(1-B)$ has the very small value 0.059. Therefore, the values of A and of b are not important. And since P_{H_2} is so small that it likewise cannot play an important role, we must, therefore, look for a reaction which decomposes HBr without the intermediate formation of H atoms. The possibility of Br_2^+ or Br^+ reacting with HBr would be inadequate to explain the observed yield unless they too decomposed HBr without the formation of atoms. The only reaction of this type is

$$HBr^+ + HBr \rightarrow H_2 + Br_2^+ - 7 \text{ kcal.} \qquad (9)$$

and this seems to be ruled out of consideration from energy considerations if the ionization potentials of HBr and of Br_2 are respectively 13.2 ev and 12.8 ev. However, the fact that Br_2^+ does not increase the yield of HBr in a hydrogen bromide mixture indicates that the reverse reaction to (9) is prevented either by endothermicity or a high energy of activation.

The preceding theory could be experimentally tested if (a) a procedure could be devised of carrying the ions to metal electrodes where they would combine without reacting and then measuring the residual reaction due to excited molecules; (b) measuring the relative rates of reaction of electrons with Br_2 and HBr to make $Br + Br^-$ and $H + Br^-$ respectively.

The discrepancies in Table III between the calculated and measured M/N yields could probably be accounted for by a consideration of reactions of the type of (8a) and (9) but we have preferred to await further investigation making more certain the reality of these discrepancies before carrying our analysis further. While clustering no doubt occurs we have regarded it as playing a very minor role. Thus the activation energy of certain reactions may be increased or lessened by a sheath of molecules in much the same way as this is accomplished for ions in solution. However, the course of reaction of the ions is governed chiefly by the same type of specific considerations important in any gas phase reactions.

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The Vapor Pressure of Potassium Chloride and Caesium Iodide Crystals

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THE measurements of Rodebush, Murray and Bixler[1] of the electric moments of the alkali halide molecules attribute a value of roughly ten Debye units to these molecules. Since this high value for the dipole moment has been calculated on the assumption of simple diatomic moeculles,

it is of importance to consider the possibility of association into at least double molecules, $(KCl)_2$. Such a molecule could conceivably have either a rhombic structure with a zero resultant moment or a linear structure with a corresponding large moment. If no association is present then the nearly 100 percent ionic nature of the alkali halide molecule is fairly well ascertained.

The vapor pressures were measured in a tem-

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[1] Rodebush, Murray and Bixler, J. Chem. Phys. 4, 372 (1936).