4. Selenous and tellurous acids in the same sample may be determined by using a combination of the dichromate and permanganate methods.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF CAMBRIDGE UNIVERSITY]

THE INFLUENCE OF WATER ON THE COMBINATION OF THE HALOGENS WITH HYDROGEN

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In a previous communication[1] evidence was presented for the assumption that the Budde effect was brought about by the photochemical dissociation of a halogen hydrate into atoms and that this process (for high water concentrations) obeys the simple Stark-Einstein law of photochemical equivalence. The quantum efficiency, however, is zero in a thoroughly dry system. If the primary chemical action in all halogen-hydrogen reactions both photochemical and thermal is the dissociation of the excited halogen molecule into atoms through interaction with water, the subsequent reactions of the atoms being dependent on the nature of the halogen and the temperature of the system, then as shown from the Budde effect, no photochemical combination in the visible portion of the spectrum should result in completely desiccated systems. Further, if water is necessary for the dissociation of photo-excited molecules, it appears probable that the same will be true for thermo-excited halogen molecules, that is, those excited by collision, and we shall obtain no thermal combination in the dry gases.[2]

A. The Hydrogen-Chlorine Reaction.—The influence of water in this system has been studied for the thermal reaction by Mellor[3] and for the photochemical reaction by Bodenstein and Dux,[4] Tramm[5] and Coehn and Jung.[6] It was shown by the latter, employing visible light, that no combination could be detected with 10^{-7} mm. of water vapor present. At 10^{-5} mm. combination occurred. Bodenstein and Dux[4] could detect no difference in velocity at 2.3 mm. and at what was believed to be 4×10^{-3} mm. Since, however, the reaction vessel was not baked out and the chlorine contained a small quantity of oxygen which undergoes photochemical hydrogenation with chlorine as optical sensitizing agent,[7] it is quite possible that the lower limit of water vapor may have been as high as 0.1 mm. We are thus uncertain how far an increase in water vapor from 10^{-5}

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[1] Lewis and Rideal, *J. Chem. Soc.*, **129**, 583, 596 (1926).

[2] From the data of Wehn and Jung it would appear that ultraviolet light, that is, a large quantum, may effect dissociation in the absence of water.

[3] Mellor, *J. Chem. Soc.*, **81**, 1272 (1902).

[4] Bodenstein and Dux, *Z. physik. Chem.*, **85**, 297 (1913).

[5] Tramm, *ibid.*, **105**, 358 (1923).

[6] Coehn and Jung, *Ber.*, **56**, 696 (1923).

[7] Norrish and Rideal, *J. Chem. Soc.*, **127**, 787 (1925).

to 0.1 mm. affects the reaction velocity. It is improbable from Coehn and Jung's experiments on reaction in dry gases under illumination with ultraviolet light that water actually enters the chain mechanism as proposed by Coehn and Jung[6] and Chapman,[8] although Weigert's[9] objection from the quantitative standpoint cannot be considered as conclusive in the light of the above data. Marshall[10] and Boehm and Bonhoeffer[11] have shown that hydrogen atoms readily react with halogen molecules, but this also cannot be considered as conclusive, for Wood[12] and Bonhoeffer[13] note that to ensure the passage of hydrogen atoms through a tube, moisture must be present to prevent the catalytic formation of molecules on the dry glass walls. Mellor[3] succeeded in stopping the thermal combination in the presence of phosphorus pentoxide at temperatures where the moist gases explode. It may be concluded that while water is essential for the process of starting a chain, it is still an open question whether water is necessary for chain propagation; the evidence available, on the whole, negatives this assumption.

B. The Hydrogen-Bromine Reaction.—In this reaction Bodenstein and Lind[14] found no alteration in velocity on the addition of water. The experimental results to be described do not agree with this conclusion and an examination of their method reveals inadequate drying. The interpretation of the reaction mechanism was given simultaneously by Christiansen,[15] Polanyi[16] and Herzfeld[17] and is based upon the following reactions.

$$Br_2 \longrightarrow 2Br \quad (1)$$

$$Br + H_2 \longrightarrow HBr + H \quad (2)$$

$$H + Br_2 \longrightarrow HBr + Br \quad (3)$$

$$H + HBr \longrightarrow H_2 + Br \quad (4)$$

$$2Br \longrightarrow Br_2 \quad (5)$$

It is assumed that equilibrium between Reactions 1 and 5 is established instantaneously. Since at ordinary temperatures Reaction 2 is somewhat endothermic (—7000 cal.) only a certain fraction of collisions between bromine atoms and hydrogen molecules is effective. Pusch[18] found at ordinary temperature only one molecule of hydrogen bromide formed for the absorption of about a thousand quanta while Lind,[19] operating at

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[8] Chapman, *Trans. Faraday Soc.*, **21**, 547 (1926).

[9] Weigert, *Z. physik. Chem.*, **106**, 426 (1923).

[10] Marshall, *J. Phys. Chem.*, **29**, 842 (1925).

[11] Boehm and Bonhoeffer, *Z. physik. Chem.*, **119**, 385 (1926).

[12] Wood, *Proc. Roy. Soc.*, **102A**, 1 (1922).

[13] Bonhoeffer, *Z. Elektrochem.*, **31**, 521 (1925).

[14] Bodenstein and Lind, *Z. physik. Chem.*, **47**, 168 (1906).

[15] Christiansen, *Kgl. Danske Videnskab. Selskab, Math.-fys. Medd.*, **1**, 14 (1919).

[16] Polanyi, *Z. Elektrochem.*, **26**, 50 (1920).

[17] Herzfeld, *ibid.*, **25**, 301 (1919); *Ann. Physik*, [IV] **59**, 135 (1919).

[18] Pusch, *Z. Elektrochem.*, **24**, 336 (1918).

[19] Lind, *J. Phys. Chem.*, **27**, 55 (1924).

250°, states that in none of his experiments did the quantum efficiency exceed that demanded by the Stark-Einstein law. Since, however, Bodenstein and Lütkemeyer[20] found a photochemical temperature coefficient at about 200° of 1.5, either a chain mechanism or an alteration in the temperature coefficient must become pronounced at elevated temperatures. Here we should anticipate, where according to Christiansen[15] the mean kinetic energy is sufficiently high to cause Reaction 2 to take place as a result of collision, that in photochemical combination the sequence Reactions 2 and 3 might occur several times (that is, a chain mechanism), especially with high pressures of hydrogen and at the commencement of reaction when hydrogen bromide is absent. The calculations in Table I, made from the data of Bodenstein and Lütkemeyer,[20] indicate that at 218° this does not yet generally occur, although at high pressures of hydrogen the quantum efficiency does begin to exceed two.

TABLE I

CALCULATIONS FROM THE DATA OF BODENSTEIN AND LÜTKEMEYER

Initial pressures: Br_2 = 146.7 mm.; H_2 = 306.3 mm.; HBr = 0

Time interval, min.	15	15	15	15	15	25	30	30	30
Total $h\nu$ absorbed $\times 10^{-19}$	2.82	2.62	2.33	2.14	1.985	2.97	3.03	2.54	2.13
Total HBr formed $\times 10^{-19}$	3.63	3.36	2.87	2.08	1.77	3.23	3.36	2.16	2.07
Moles/$h\nu$	1.28	1.28	1.22	0.975	0.89	1.09	1.11	0.85	0.97

Initial pressures: Br_2 = 152.9; H_2 = 310.1; HBr = 0

Time interval, min.	15	10	15	30	20	20	40	60
Total $h\nu \times 10^{-19}$	2.96	1.85	2.62	4.66	2.72	2.42	4.06	4.75
Total HBr $\times 10^{-19}$	3.40	2.08	2.67	4.36	2.93	2.23	3.76	4.16
Moles HBr/$h\nu$	1.15	1.13	1.02	0.935	1.08	0.925	0.925	0.875

Initial pressures: Br_2 = 136.4; H_2 = 438.6; HBr = 0

Time interval, min.	15	15	20	30	20	20
Total $h\nu \times 10^{-19}$	2.67	2.37	2.69	3.29	1.8	1.495
Total HBr $\times 10^{-19}$	4.45	4.01	3.82	4.58	2.64	2.04
Moles HBr/$h\nu$	1.67	1.69	1.42	1.39	1.47	1.36

Initial pressures: Br_2 = 102.2; H_2 = 507.2; HBr = 69.0

Time interval, min.	10	10	20	30	30
Total $h\nu \times 10^{-19}$	1.41	1.22	2.02	2.15	1.48
Total HBr $\times 10^{-19}$	3.52	2.76	4.64	4.77	2.28
Moles HBr/$h\nu$	2.5	2.27	2.30	2.21	1.55

Initial pressures: Br_2 = 136.5; H_2 = 507; HBr = 0

Time interval, min.	10	10
Total $h\nu \times 10^{-19}$	1.79	1.62
Total HBr $\times 10^{-19}$	3.88	3.82
Moles HBr/$h\nu$	2.17	2.36

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[20] Bodenstein and Lütkemeyer, *Z. physik. Chem.*, **114,** 208 (1924).

As Table II shows for nearly identical concentrations of bromine, the quantum efficiency varies as the hydrogen pressure. In other words, the efficiency of the whole process is limited by Reaction 2.

TABLE II

Hydrogen pressure, mm.	308	439	507
Quantum efficiency	1.21	1.68	2.17
H_2 pressure/quantum efficiency	254	261	234

These data support the view that the chemical reaction takes place through the medium of bromine atoms and since it was shown in the Budde effect that dissociation of excited molecules occurs only in the presence of water vapor it was anticipated that no combination would take place in the dry gases.

The apparatus employed is shown in Fig. 1.

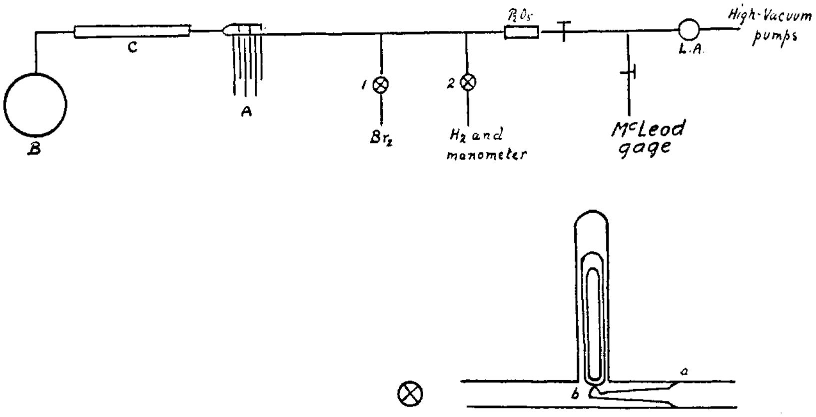

Fig. 1.

A consists of six glass bulbs each 1 cm. in diameter and about 6 cm. long. These were connected on one side to C, a 20 cm. length of 2cm. glass tubing into which phosphorus pentoxide could be freshly distilled under a high vacuum from the glass bulb B, and on the other side, to the bromine and hydrogen reservoirs through the inside scales 1 and 2 (shown enlarged). This modification of fracturing a small thin bulb instead of a capillary proved much more satisfactory since it is sometimes impossible to break the latter on account of its resiliency. The hydrogen and bromine reservoirs were separated from the rest of the system while the reaction bulbs were being baked out. The remainder of the apparatus consisted of a small phosphorus pentoxide tube to absorb moisture removed during the baking out, a stopcock, a McLeod gage with stopcock for measuring low pressures, a liquid-air trap to prevent back diffusion of mercury vapor and a high-vacuum system which consisted of two mercury-diffusion pumps in series with a motor-driven oil pump. Between B and C, C and A, A and 1, A and 2, and A and the phosphorus pentoxide tube the glass was constricted to facilitate sealing off with a blow pipe. Each bulb in A could be removed separately by the same arrangement.

For all except the last set of experiments no phosphorus pentoxide was distilled into the reaction bulb. The system B and C was therefore dispensed with.

The bromine used was very dry, being the same used in the Budde effect experiments[1] and by this time had been dried for nearly one and one-half years. Care was taken to remove all oxygen by pulling bromine vapor through the reservoir for some time by means of side pieces leading to a water pump carefully protected by drying tubes. The hydrogen reservoir consisted of a phosphorus pentoxide drying train of about 500-cc. capacity and a mercury manometer. After several evacuations, hydrogen from a cylinder was passed through this for one day to insure removal of all oxygen. The small amount of oxygen originally in the hydrogen was removed by passing the gases over heated copper turnings, the water formed being removed by a drying train before entering the hydrogen reservoir. Before each experiment the dry hydrogen had remained in the latter for several days.

The experimental procedure was as follows: a high vacuum (less than 10^{-6} mm. of mercury) was maintained on the system for two days while the reaction bulbs were baked out in a furnace at 420°. The glass tubing out of the furnace was frequently and thoroughly baked out with a Bunsen flame. Fresh phosphorus pentoxide was distilled from B to C, the former sealed off and the furnace removed. The phosphorus pentoxide was then distilled into each of the reaction bulbs such that a thin, fluffy layer possessing excellent drying properties coated the surface. The ends were kept free of phosphorus pentoxide to permit penetration of radiation from the light source. The pumps were kept working for about an hour, after which they, as well as C, were sealed off. The bromine reservoir had been maintained at a definite temperature to give the desired partial pressure of bromine (determined from the data of Ramsay and Young in Landolt-Börnstein "Tabellen") and Seal 1 fractured by lifting the iron core, encased in glass, with a magnet. One hour being allowed for equilibrium to establish itself, the reservoir was then sealed off. In a similar manner hydrogen was admitted and the total pressure (hydrogen and bromine) read on the manometer. Finally, each bulb was sealed off separately after allowing a day for equilibrium to establish itself.

A bulb was placed horizontally on an arrangement in the center of the furnace, which part could be kept uniform to one degree, and the reaction was carried out at elevated temperatures supplemented or not with radiation from a 1000-candle power lamp (1.9 amps., 220 volts) placed 33 cm. from the end of the bulb.

Analysis was made for the quantity of bromine left, comparing the final with the initial concentration determined in an untreated bulb. This was accomplished by breaking the tip under potassium iodide solution and the iodine was titrated with carefully standardized thiosulfate solution (0.00978 *N*). In those experiments where phosphorus pentoxide was not distilled into the bulb, the hydrogen bromide was estimated with sodium hydroxide solution (0.01128 *N*) standardized against a hydrochloric acid solution whose titration value against barium hydroxide solution was known. The latter was standardized with pure succinic acid. The volume of each bulb was determined. In this way the total bromine in each reaction was estimated and therefore the percentage conversion into hydrogen bromide.

The following results are those of experiments in which no phosphorus pentoxide was distilled into the reaction vessel. It may be stated at the onset that in nearly all of them there was every indication of the reaction being slowed. In view of the later experiments with a drying agent where the reaction was stopped practically completely, one recognizes the difficulty in obtaining perfectly dry vessels in which a reaction is to be carried out at high temperatures where the rate of diffusion of moisture from the interior of the glass is appreciable. In the first three runs, vessels of 67 to 73 cc. capacity were employed. In the last column but one the percentage conversion obtained by Bodenstein and Lind[14] for the thermal reaction is given for comparison wherever possible.

TABLE III

EXPERIMENTS WITHOUT PHOSPHORUS PENTOXIDE

Expt.	Press. of Br_2, mm.	Press. of H_2, mm.	Temp., °C.	Light on	Time, hours	Conversion, %	Conversion, %
1	153	506.1	23.5	yes	42	13.72	....
2	150	509.1	100	yes	20.5	11.10	....
3	131	558	100	yes	12	4.45[a]	....
4	177	399	250	no	2	0.3	6.25
5	180	399	250	yes	2	1.51	....
6	199	437	250	no	4	5.33	11.6
7	152	484.3	250	yes	4	54.5	....
8	184	452.3	275	no	4	48.8	52.2
9	186	450.3	275	yes	4	82.6	....
10	147	512.1	275	no	4	56.9	....
11	1 4.0	463.4	300	yes	2	86.0	(Ca) 52.2
12	221	415.3	300	no	1	42.3	61.3
13	167	469.3	300	yes	1	79.4	....

[a] Moist.

A comparison of the percentage conversion columns points to a marked retardation in the reaction rate. Expts. 4 and 5 show that almost no reaction has occurred (compare 5 with 9 and 11, etc.). However, it was impossible to duplicate this effect. In fact, it was practically impossible to obtain the same degree of dryness even in experiments where the reaction vessels were treated under the same conditions. Expts. 1, 2 and 3 show that the photochemical combination occurs at ordinary temperatures with a velocity that can be measured. However, the quantum efficiency must be extremely low, which is in agreement with Pusch.[18]

Table IV shows the results of experiments in which phosphorus pentoxide had been distilled into the reaction vessels. Hydrogen bromide could not be estimated and it was found by separate tests that the presence of phosphorus pentoxide in no way affected the estimation of bromine.

TABLE IV

EXPERIMENTS WITH PHOSPHORUS PENTOXIDE

Original press. of Br_2, mm.	Press. of H_2, mm.	Temp., °C.	Light on	Time, hours	Final press. of Br_2, mm.	Conversion, %	Remarks
151	468	275	yes	4	153	nil	Conversion of moist sample would be about 67.5%. Error in obtaining bulb volume about 2%
151	468	325	yes	3	147	2.6	Conversion of moist sample would be 100% in less than 1 hour
151	468	400	yes	2	142.6	5.56	Conversion of moist sample would be 100% in less than 5 minutes

These experiments prove conclusively that the thermal and photochemical combination is stopped completely in the absence of water vapor over the temperature range used by Bodenstein and Lind,[14] while even at higher temperatures it proceeds at a rate that is negligible in comparison with the rate of combination of moist gases under the same conditions.

We may conclude that in the thermal combination of hydrogen and bromine the first reaction is the formation of excited bromine molecules by collisions between rapidly-moving bromine molecules. The second action is the dissociation into atoms of the excited bromine molecules on collision within their mean lifetime with water molecules and finally the reaction of the bromine atoms thus produced either with hydrogen molecules or more rarely, at high hydrogen pressures, with bromine atoms. The relationship between the mean life of the excited bromine molecules and the necessary water vapor pressures may be determined from the experimental data of Bodenstein and Lind.[14]

At T = 574°K., C = 0.2278 mole per 22.4 liters, the reaction-velocity constant was found to be 0.0851/60 with the second as unit of time. Hence, the rate at which bromine disappears by combination with hydrogen at one atmosphere is

$$-\mathrm{d}N/\mathrm{d}t = (6.06 \times 10^{23}) \times 0.2278 \times (0.0851/60) = 1.93 \times 10^{20} \text{ molecules per 22.4 liters per second} \quad (6)$$

To calculate the rate of excitation or activation of bromine molecules per second by the reaction $Br_2 + Br_2 \longrightarrow Br'_2 + Br_2$, we employ the general expression[21] for bimolecular collisions between molecules each containing f squared terms (of internal energy).

$$\mathrm{d}N'/\mathrm{d}t = N^2\sigma^2 \sqrt{\frac{4\pi RT}{m}}\, e^{-\frac{E}{RT}} \frac{\left(\frac{E}{RT}\right)^{f+1}}{(f+1)!} \quad (7)$$

In the case of bromine at 574°K., $\sigma = 3.2 \times 10^{-8}$ cm., $E/RT = 40, f = 4$

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[21] See discussion at the British Association at Oxford, 1926, for applications of this equation.

(the bromine molecule being fully excited and containing two rotational and two oscillational squared terms). Inserting the value $N = 0.2278 \times 6.06 \times 10^{23}$ we obtain

$$dN'/dt = 6.95 \times 10^{20} \text{ molecules per 22.4 liters per second} \tag{8}$$

If the life of an excited bromine molecule be τ the concentration of excited bromine molecules is

$$N' = 6.95 \times 10^{20}\, \tau \text{ molecules per 22.4 liters} \tag{9}$$

According to the hypothesis only those excited bromine molecules dissociate into atoms (and these can enter into combination with hydrogen) which collide with a water molecule within their lifetime.

If the partial pressure of water be P mm., then the number of collisions between excited bromine molecules and water molecules per second will be

$$\frac{dN_2}{dt} = N' \frac{6.06 \times 10^{23}}{760} P\, \sigma\sigma_2 \sqrt{2\pi RT \frac{1}{m} + \frac{1}{m_2}} \tag{10}$$

This rate is identical at the beginning of the reaction with the rate of formation of atoms and can be equated to the rate of formation of hydrogen bromide or

$$dN_2/dt = dN/dt \tag{11}$$

Inserting the values from Equations 6, 9 and 10 in 11 and placing[22] $\sigma_2 = 4.54 \times 10^{-8}$ cm. and $m_2 = 18$ we obtain $\tau P = 1.14 \times 10^{-8}$. According to Wien and Dempster the life of an excited molecule is τ = about 10^{-7} seconds, hence $P = 10^{-1}$ mm. = 0.1 mm. as the water-vapor pressure necessary for the hydrogen bromine reaction to attain its maximum velocity under the above-mentioned conditions. We have already noted that the experimental evidence indicates that the reaction does not cease suddenly as drying is proceeded with, and a value of 0.1 mm. for the water-vapor pressure is by no means unlikely for the conditions of maximum velocity.

C. The Hydrogen-Iodine Combination.—In this reaction the work of Bodenstein[23] on the combination, dissociation and equilibrium has been taken by Hinshelwood[24] to be the most perfect example of the principle of activation by collision, the simple reaction mechanism $H_2 + I_2 \rightleftarrows 2HI$ being postulated.

A number of arguments may be advanced in criticism of this view. Bodenstein[23] gives the following equilibrium percentage decomposition of hydriodic acid under various conditions of pressure and temperature.

Temp., °C.	0.5 atm.	1.0 atm.	1.5 atm.	2 atm.
518	22.51	23.63	24.12	24.43
448	20.19	21.43	22.25	23.06
350	13.49	17.63	19.20	19.87

It is clear that pressure influences the equilibrium, and it must be assumed

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[22] Jeans, "The Dynamical Theory of Gases."

[23] Bodenstein, *Z. physik. Chem.*, **13**, 56 (1894); **29**, 245 (1899).

[24] Hinshelwood, "Kinetics of Chemical Change in Gaseous Systems," pp. 48–58.

either that the activity of the iodine is not proportional to its partial pressure or that the simple mechanism postulated is not the correct one.

If iodine vapor be considered ideal at 448° and 25.8 mm., the activity coefficient would have to be as small as 0.71 at 150 mm., the corresponding value at 350° being no greater than 0.395. Again, it will be noted that in the combination of both chlorine and bromine with hydrogen, dissociation into atoms has been postulated for diverse reasons. There seems to be no *a priori* reason why this should not be the case with iodine also. Since iodine molecules are relatively unsaturated, forming compounds such as the poly-iodides, we might anticipate that equilibrium in iodine vapor could be represented by the following reactions

$$\mathrm{I_2} \rightleftharpoons \mathrm{2I} \qquad (12)$$
$$\mathrm{I + I_2} \rightleftharpoons \mathrm{I_3} \qquad (13)$$
$$\mathrm{I_3 + I} \rightleftharpoons \mathrm{2I_2} \qquad (14)$$

and that the main reaction involved in hydrogenation at low temperatures might be

$$\mathrm{I_3 + H_2} \longrightarrow \mathrm{2HI + I} \qquad (15)$$

in addition to the less frequent and more highly endothermic reaction,

$$\mathrm{I + H_2} \longrightarrow \mathrm{HI + H} \qquad (16)$$

thus differing from the hydrogen-bromine combination. Since the removal of I_3 molecules can take place by Processes 14 and 15, the reaction velocity will be given by $dC/dt = -K[(C_{H_2})(C_{I_3})]/(C_{I})$, and from Reaction 13, $dC/dt = -K'[(C_{H_2})(C_{I_2})(C_{I})/(C_{I})] = -K'(C_{H_2})(C_{I_2})$, which is the experimental result of Bodenstein.

Bodenstein suspected that iodine atoms might play a part in the reaction and made a determination of the vapor density at 448°. Instead of obtaining a smaller value than the theoretical one of 8.765, he obtained 8.908. This not inconsiderable increase in density might be explained on the assumption of the presence of a complex including I_3 molecules; it is also evidently an insufficient increase in density if iodine vapor departs from the perfect gas laws to the extent demanded by the hypothesis referred to above.

If the formation of iodine atoms is the primary step in the formation of hydrogen iodide, then from the postulate advanced here that the effect of the absence of water vapor is to prevent dissociation, we should expect that under very dry conditions no hydrogen and iodine would combine. Initial experiments were undertaken to confirm Coehn and Tramm's[25] observations that hydrogen iodide, even when dry, undergoes thermal decomposition.

Hydrogen iodide was prepared from pure hydrogen and pure iodine by passing them over heated platinized asbestos according to the method outlined by Bodenstein.[23] Care was taken to freeze out all the excess iodine,

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[25] Coehn and Tramm, *Ber.*, **56B**, 458 (1923).

the hydrogen iodide passing on and to a liquid-air trap. It was purified by two low-temperature distillations and finally allowed to expand through a drying train into a dry, blackened glass bulb (1 liter) whose inner surface was covered with phosphorus pentoxide. The bulb, which was already fitted with an inner-seal arrangement, was joined to an apparatus similar to that described above in the experiments on hydrogen and bromine. Small bulbs were thoroughly baked out and lined with distilled phosphorus pentoxide as before, and finally after a week of drying, the hydrogen iodide was allowed to enter. Each bulb was sealed off and the reaction carried out at elevated temperatures. One bulb was analyzed without allowing any reaction, to obtain the initial pressure of hydrogen iodide. This was done by the standard method of oxidizing the acid to iodine and distilling the latter into potassium iodide, after which this was titrated with sodium thiosulfate solution. The reacting bulbs were analyzed for iodine. In each case, on breaking the tip of the bulb under the absorbing solution, there was a residual gas present, indicating hydrogen. The results are summarized in Table V.

Table V

Reaction under Very Dry Conditions

Temp. of reaction: 432°. Time, one hour. Original pressure of HI, 404 mm.

Reaction bulb No.	HI decomp., mm.	Decompn., %
1	396	98
2	402	99.5
3	356	88.0

This result was startling since the equilibrium value at this temperature and pressure in ordinary unbaked vessels represents about 19.5% decomposition. Several moist reaction bulbs were filled with hydrogen iodide and the extent of the reaction was determined after one hour at the same temperature. The results agree with Bodenstein's value, the average decomposition being 17.5%. The simplest interpretation of the results is that the decomposition of hydriodic acid may proceed in the absence of water, but that the recombination of the elements is not a simple bimolecular process. Under conditions of intensive desiccation or in the presence of solid phosphorus pentoxide, the equilibrium is shifted, the reversible process being rendered irreversible.

This interpretation is given with some diffidence, as this would be the first example of a reversible system in which a catalyst does not affect the reaction velocities of each reaction to equal extents. Similar conclusions can of course be drawn from the work of Baker and Smits on inner equilibrium in desiccated systems. It would be desirable to devise experiments in which complete desiccation in the absence of phosphorus pentoxide could be effected, although it is difficult to see how the active mass of the iodine can be reduced by this material so as to permit of such a marked shift of the equilibrium.

In support of the hypothesis that the formation of hydrogen iodide is not a simple bimolecular reaction may be cited the results of photochemical investigation. According to the view expressed above, the velocity of reaction in the combination of hydrogen with bromine and with iodine is governed by the velocities of the endothermic reactions (a) $H_2 + Br \longrightarrow HBr + H$; (b) $H_2 + I_3 \longrightarrow 2HI + I$; (c) $H_2 + I \longrightarrow HI + H$.

In the case of the combination of hydrogen and chlorine, the reaction $H_2 + Cl$ is strongly exothermic, the primary chemical reaction in all cases being the dissociation of the halogens. For identical quanta absorption in the reactions with bromine and iodine the velocities will be dependent on the probabilities of Reactions a, b and c occurring. Since the iodine reaction is more endothermic than the bromine reaction, the photochemical union of hydrogen and iodine should proceed more slowly than that of the hydrogen and bromine but the rate or quantum efficiency should, as in the case of the bromine reaction, increase with elevation of the temperature.

Coehn and Stuckardt[26] have shown that hydrogen iodide is formed by illumination of the reactants in a quartz vessel with a quartz-mercury lamp at ordinary temperatures. No formation, however, was observed with a Uviol or Jena glass vessel. Bowen[27] did not detect any photochemical formation in glass bulbs at ordinary temperatures. At high temperatures, however, as we have noted, combination might be expected to occur. That this does take place is evident from the following experimental data.

Several small bulbs were filled with hydrogen iodide and exposed to radiation of wave length longer than 4600 Å. (Wratten light filter 8) from a 1000-candle power lamp. Such light is not absorbed by hydrogen iodide. The bulbs were heated to 430° and 466°, respectively. After an hour they were rapidly cooled and the contents analyzed both for iodine and hydriodic acid.

TABLE VI

REACTION AT HIGH TEMPERATURES

Temp., °C.	Initial HI, moles per l.	Light on	Final HI, moles per l.	Moles of $I_2 \times 2$ per l.	Decompn., %
430	0.03030	No	0.02483	0.00542	17.9
430	.03022	Yes	.02557	.00465	15.35
466	.02923	No	.02157	.00767	26.2
466	.02922	Yes	.02210	.00711	24.3
466	.02986	Yes	.02250	.00738	24.7

A very definite shift in the thermal equilibrium is produced by illumination of the system with light absorbed by the iodine at temperatures of 430° and 466°.

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[26] Coehn and Stuckardt, *Z. physik. Chem.*, **91,** 722 (1916).

[27] Bowen, *J. Chem. Soc.*, **125,** 1233 (1924).

Summary

The influence of water on the halogen-hydrogen combinations is discussed. Reasons are advanced for the hypothesis that the primary chemical reaction takes place between halogen atoms and hydrogen. Halogen molecules excited either by light in the visible portion of the spectrum or by thermal collision do not dissociate into atoms except on collision with water molecules. While dissociation does not affect the thermal decomposition of hydrogen iodide, the thermal and photochemical union of hydrogen and bromine and the thermal combination of hydrogen with iodine can be stopped by desiccation.

In the combination of hydrogen and bromine the commencement of the chain mechanism, so marked in the hydrogen-chlorine reaction, can be detected at high temperatures and high pressures of hydrogen. The relationship between the mean life of the excited bromine molecule and the water-vapor pressure required for the attainment of a velocity maximum of combination is developed. With a value of $\tau = 10^{-7}$ sec., this pressure is found to be of the order of 0.1 mm. A mechanism for the combination of hydrogen with iodine based upon the primary dissociation of iodine into atoms is advanced and this system is shown to be photochemically sensitive at high temperatures (450°) in accordance with theoretical considerations. It is considered unnecessary to assume that the chain mechanism involves water.

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[CONTRIBUTION FROM THE BUREAU OF MINES, UNITED STATES DEPARTMENT OF COMMERCE, PACIFIC EXPERIMENT STATION, AND THE CHEMISTRY DEPARTMENT OF STANFORD UNIVERSITY]

THE FREE ENERGY OF FORMATION OF ZINC OXIDE[1]

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This article is the last of three dealing with the free energy of formation of zinc oxide. Four possible methods of experimentally determining the standard free energy of stable oxides usually are available: (1) measurement of high-temperature equilibria and extrapolation of the results; (2) measurements dependent on the electromotive force of reversible galvanic cells; (3) calculation from low-temperature specific-heat data and the third law of thermodynamics; (4) calculation from solubility values and standard electrode potentials. The present work reports new experimental results

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