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EMISSION SPECTRUM OF THE FLAME OF BROMINE BURNING IN HYDROGEN AND MECHANISM OF THE REACTION*.

By Tetsuzô Kitagawa.

In the preceding paper[1] it was reported that in the emission spectrum of the flame of chlorine burning in hydrogen some emission bands were found, which were ascertained to belong to the excited chlorine molecules, and the mechanism of the combustion reaction between chlorine and hydrogen was discussed from these results.

In the combustion of bromine in hydrogen a number of emission bands belonging to the excited bromine molecules were found. In the present paper the mechanism of the reaction between bromine and hydrogen will be discussed from this fact.

[I] The Emission Spectrum of the Flame of Bromine in Hydrogen.

(i) Apparatus

The apparatus used is shown in Fig. 1. Purified hydrogen was introduced through a flow-meter and the side tube *e* into the quartz vessel *a*, 3 cm. in diameter and 10 cm. in length, and the excessive hydrogen and the hydrogen bromide formed by combustion were expelled through the other side tube *d*. Bromine vapour was let flow out through *g* and *h* at a constant velocity, the temperature of the reservoir of liquid bromine *b* being kept constant above the boiling point of bromine (58.7°C.) by means of the electric current on nichrome wire (BS, No. 38) coiled round it. The tube *g*-*h* was specially made of quartz. The method to light the flame of bromine was the same as that of the preceding report[1].

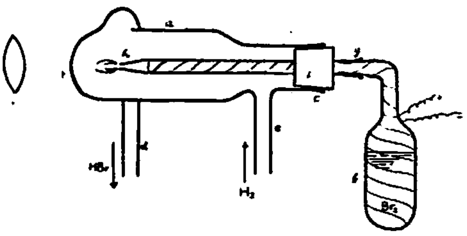

Fig. 1. The Main Part of the Apparatus.

No grease was used on the passage of the bromine vapour and only the ground part *g* was joined with a small quantity of viscous phosphoric acid.

The same glass spectrograph was used as in the preceding experiment[1]. The

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* This paper is the English translation of the same article published in *Rev. Phys. Chem. Japan*, 10, 1 (1936).

[1] T. Kitagawa, *Rev. Phys. Chem. Japan*, 8, 71 (1934); 11, 61 (1937).

dispersion of the spectrograph was 12 Å/mm at 4500 Å and 45 Å/mm at λ 5900 Å. The Ilford Hypersensitive Panchromatic Plates were also used.

(ii) Temperature of the flame

The temperature of the flame was measured by means of a thermoelement with platinum-platinum rhodium alloy, which indicated the temperatures of about 480°~500°C. There was some reason to believe that the temperature of the flame was somewhat higher than this. It was proved, however, that the temperature of the flame of bromine was relatively low compared with the flame of chlorine which had been about 1000°C.

(iii) Emission spectrum of the flame

The flame was visibly of orange colour. The emission spectrum of the flame is shown in Plate I, the time of exposure being about 1 hour. In Plate I about

Table I.

Band-Heads in the Emission Spectrum of the Bromine-Hydrogen-Flame.

No.	Wave length λ, Å	Wave number ν, cm⁻¹	Int.	No.	Wave length λ, Å	Wave number ν, cm⁻¹	Int.
1	6875	14541	0	23	6142	16276	6
2	6801	14700	1	24	6120	16334	4
3	6744	14823	3	25	6097	16398	5
4	6729	14857	3	26	6072	16466	4
5	6675	14978	5	27	6056	16508	2
6	6667	14995	5	28	6024	16596	4
7	6605	15135	7	29	5982	16712	4
8	6593	15163	7	30	5957	16781	3
9	6548	15269	8	31	5941	16827	3
10	6532	15305	8	32	5910	16916	5
11	6474	15443	10	33	5867	17039	5
12	6417	15579	10	34	5831	17146	4
13	6406	15605	6	35	5802	17230	1
14	6360	15719	9	36	5794	17254	3
15	6342	15763	7	37	5761	17354	2
16	6313	15836	8	38	5753	17377	1
17	6290	15893	9	39	5724	17467	2
18	6264	15961	6	40	5692	17563	1
19	6240	16021	8	41	5660	17663	1
20	6220	16072	3	42	5629	17762	1
21	6189	16155	7	43	5600	17852	0
22	6168	16209	5				

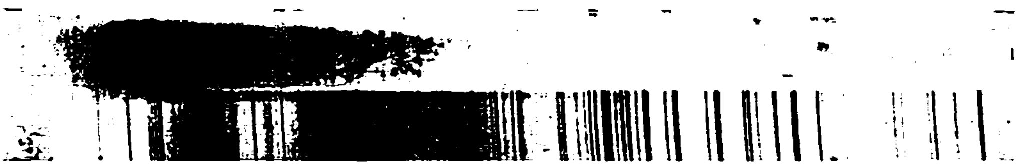

Plate I.

The Emission Spectrum of the Flame (Ref., Fe-arc spectrum).

43 emission bands are observed in the range $\lambda\lambda$ 6880∼5000 Å. The fine structure of each band is obscure, but the band-head is distinctly observed, and all the bands shade to the red. The band-heads of these emission bands were measured, being referred to the Fe-arc spectrum. In Table I are given the wave-length λ, the wave number in vacuum ν and the intensity roughly estimated.

(iv) The carrier of the emission bands

From the fact that the emission band system in Plate I is relatively of simple structure it is probable that the carrier of the spectrum is a diatomic molecule. The diatomic molecules present in the flame are hydrogen, hydrogen bromide and bromine. The band spectrum belonging to hydrogen is known as many lined spectrum which exhibits innumerable emission lines and is not of an ordinary band form. Hydrogen bromide has a continuous spectrum as far as we know. Weizel, Wolff and Binkele[2] found in the discharge tube of hydrogen bromide a wavy continuous spectrum in the ultraviolet region, but no emission spectrum corresponding to this could be found in the flame of bromine and hydrogen. It is evident, therefore, that the emission bands in the flame do not belong to these two kinds of molecules. Accordingly, it is considered that the carrier of the bands will be the bromine molecule.

Many researches on the absorption spectrum of bromine vapour have been made. Let us compare the absorption band of bromine with the emission band of the flame in question. The wave length of the absorption band of bromine was measured by Kuhn[3], Nakamura[4] and lately Brown[5]. In Table II are given the wave number by Brown and that of the emission band by the author in the second and the third column resp. Comparing these values it is found that both wave numbers coincide well with each other within the experimental error. This leads to the conclusion that the emission spectrum of the flame is ascribed to the bromine

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[2] W. Weizel, H. W. Wolff u. H. E. Binkele, *Z. physik. Chem.* [B], **10**, 459 (1930).

[3] H. Kuhn, *Z. Physik*, **39**, 77 (1926).

[4] G. Nakamura, *Mem. Coll. Sc. Kyôto Imp. Univ.* [A], **9**, 335 (1926).

[5] W. G. Brown, *Phys. Rev.*, **38**, 1179 (1931); **39**, 777 (1932).

Table II.

Comparison of the Absorption Bands of Bromine with the Emission Bands of the Flame.

No.	Absorption bands of bromine (by G. Brown) cm^{-1}	Vibrational quantum number (v', v'')	Emission bands of the flame (by the author) cm^{-1}	Calculated value cm^{-1}	Difference cm^{-1}
1			14541	14552.4	11
2_1			14700	14694.4	−6
2_2			14700	14714.6	15
3			14823	14832.9	10
4			14857	14860.1	3
5			14978	14967.8	−10
6			14995	15002.1	7
7			15135	15140.6	6
8	15169.2	(6,5)	15163	15170.2	7
9			15269	15275.5	7
10	15311.6	(7,5)	15305	15312.2	7
11	15450.0	(8,5)	15443	15450.7	8
12	15585.5	(9,5)	15579	15585.6	7
13	15624.6	(7,4)	[15605]	15624.6	20
14	15714.7	(10,5)	15719	15716.8	−2
15	15762.6	(8,4)	15763	15763.1	0
16	15845.1	(11,5)	15836	15544.3	8
17	15898.8	(9,4)	15893	15898.0	5
18	15967.2	(12,5)	15961	15969.1	8
19	16029.4	(10,4)	16921	16029.2	8
20	16078.4	(8,3)	16072	16077.7	6
21	16156.4	(11,4)	16155	16156.7	2
22	16214.0	(9,3)	16209	16212.6	4
23	16278.9	(12,4)	16276	16281.5	6
24	16343.4	(10,3)	16334	16343.8	10
25	16401.4	(13,4)	16398	16400.5	3
26	16472.2	(11,3)	16466	16471.3	5
27	16517.5	(14,4)	16508	16516.6	8
28	16594.4	(12,3)	16596	16596.1	0
29	16718.7	(13,3)	16712	16715.1	3
30	16789.1	(11,2)	16781	16788.3	7
31	16831.5	(14,3)	16827	16831.2	4
32	16912.9	(12,2)	16916	16913.1	−3
33	17033.7	(13,2)	17039	17032.1	−7
34	17150.0	(14,2)	17146	17148.2	2
35			17230	17232.3	2
36	17259.8	(15,2)	17254	17260.4	6
37	17353.3	(13,1)	17354	17351.3	−3
38	17368.4	(16,2)	17377	17368.8	−8
39_1	17472.1	(17,2)	17467	17473.0	6
39_2	17467.1	(14,1)	17467	17467.4	0
40_1	17572.0	(18,2)	17563	17573.1	10
40_2	17579.4	(15,1)	[17563]	17579.6	17
41	17667.6	(19,2)	17663	17669.1	6
42	17759.9	(20,2)	17762	17761.0	−1
43	17845.8	(21,2)	17852	17848.6	−3

molecule. This conclusion is also supported by the fact that both the emission band of the flame and the absorption band of bromine shade to the red region.

(v) On the emission band of bromine

Few studies on the emission band of bromine have been done as compared with those on its absoption band, and any emission band system of bromine which coincides well with the absorption has not yet been found[6] in the discharge tube.

According to Urey and Bates[7], a faint band spectrum in the range between $\lambda\lambda$ 4250 and 4675 Å was found in the flame of oxygen which contained bromine burning in hydrogen, and the spectrum was considered to belong to a compound of oxygen and halogen. In the present experiment, however, any such emission band was not observed in the wave length range.

According to R. S. Mulliken[8], the emission band of bromine in the flame (Plate I) shoud be due to the electron transition from the Ou^+ state to the $^1\Sigma_g^+$ state, for the normal state of a bromine molecule is $^1\Sigma_g^+$ and its excited state Ou^+. Accordingly, the excited bromine molecules in the Ou^+ state must be generated in the flame.

Before we consider how the bromine molecules are excited by the chemical reaction in the flame, let us calculate from a band-head analysis the vibrational energy which is possessed by the excited bromine molecule in the Ou^+ state.

[II] Band-Head Analysis and $U(r)$-Curves of Br_2.

(i) Band-head analysis of the emission band

The band-heads in the emission spectrum (Table I) were analysed and the results obtained are given in Table III, where the unit is given in cm^{-1} and the intensity is indicated in parentheses. v' and v'' in Table III are the vibrational quantum numbers of the excited and the normal states of the bromine molecule respectively, and these values have been determined in the isotopic displacement of the absorption bands by Brown.

From the band-head analysis it is seen that the emission bands of bromine in the flame have been emitted by the transition from the vibrational states $v'=$

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6) Y. Uchida and Y. Ota, *Jap. J. Phys.*, 5, 59 (1928).

7) H. C. Urey and J. R. Bates, *Phys. Rev.*, 34, 1541 (1929).

8) R. S. Kulliken, *Rev. Mod. Phys.*, 4, 1 (1932).

8a) W. M. Vaidya has lately observed in the flame of ethyl bromide the emission bands of bromine which coincide with the present author's (*Proc. Ind. Acad. Sci.* [A], 7, 321 (1938)).

Table III.

Band Analysis of the Emission Bands in the Flame. [Br_2, $Ou^+ \rightarrow {}^1\Sigma g^+$]
(v' and v'' are the vibrational quantum numbers of the excited and the normal states respectively.)

v' \ v''	1	2	3	4	5	6	7	
5						14700(1)		$^1\Sigma g^+$
6					15163(7)	14857(3)	14541(0)	
7				15605(6)	15305(8)	14995(5)	14700(1)	
8			16072(3)	15763(7)	15443(10)	15136(7)	14823(3)	
9			16209(5)	15893(9)	15579(10)	15269(8)	14978(5)	
10			16334(4)	16021(8)	15719(9)			
11		16781(3)	16465(4)	16155(7)	15836(8)			
12	17230(1)	16916(5)	16596(4)	16276(6)	15961(6)			
13	17354(2)	17039(5)	16712(4)	16398(5)				
14	17467(2)	17146(4)	16827(3)	16508(2)				
15	17563(1)	17254(3)						
16		17377(1)						
17		17467(2)						
18		17563(1)						
19		17663(1)						
20		17762(1)						
21		17852(0)						
22								
	Ou^+							

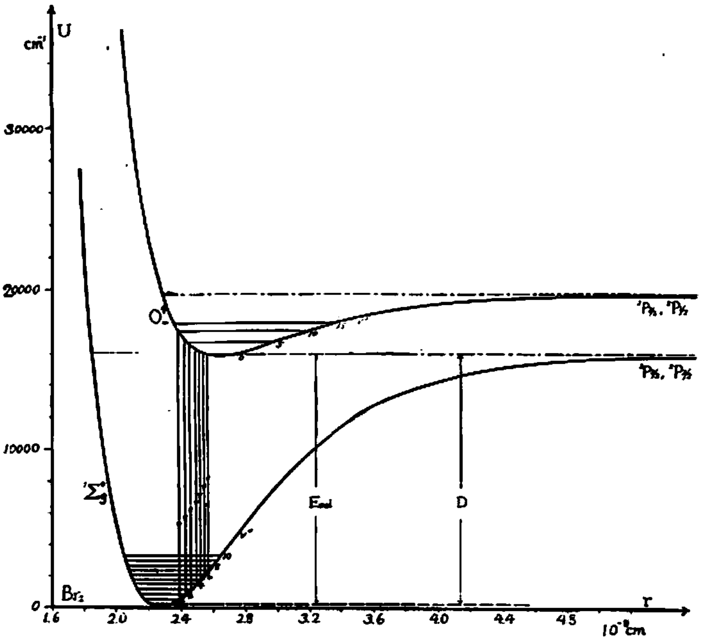

Fig. 2. $U(r)$-Curves of the Br_2 molecule.

$5 \sim 21$ in the excited state to $v'' = 1 \sim 7$ in the normal state. Thus, the vibrational quantum numbers v' and v'' of the emission bands could be determined as follows:

$$v' = 5,\ 6,\ 7, \ldots\ldots, 21\ ; \qquad v'' = 1,\ 2,\ 3, \ldots\ldots, 7. \qquad (1)$$

Table IV.

Simplified Expression of the Band Analysis of Bromine in the Transition $O_u^+ \rightleftarrows {}^1\Sigma_g^+$.

○ Observed in the absorption spectrum by G. Brown.

+ Observed in the emission spectrum of the Br_2-H_2-flame by the author.

v' \ v''	0	1	2	3	4	5	6	7
0								
1								
2								
3								
4					○			
5					○		+	
6			○	○	○	⊕	+	+
7			○	○	⊕	⊕	+	+
8			○	⊕	⊕	⊕	+	+
9			○	⊕	⊕	⊕	+	+
10			○	⊕	⊕	⊕		
11			⊕	⊕	⊕	⊕		
12		+	⊕	⊕	⊕	⊕		
13		⊕	⊕	⊕	⊕			
14		⊕	⊕	⊕	⊕			
15	○	⊕	⊕					
16	○	○	⊕					
17	○	○	⊕					
18	○	○	⊕					
19	○	○	⊕					
20	○	○	⊕					
21	○	○	⊕					
22		○						
23	○	○						
24	○	○						
⋮	⋮	⋮						
48	○							

The wave number ν of the bromine bands can be expressed by the following formula given by Brown:

$$\nu = 15831.2 + (163.81v' - 1.59v'^2 - 0.0087v'^3) - (322.71v'' - 1.15v''^2) \text{ cm}^{-1}. \qquad (2)$$

The calculated wave numbers being substituted the values of v' and v'' (1) in formula (2) are given in the fourth column of Table II, which coincide well with the wave numbers of emission bands of the flame in the third column.

In Table IV the bands observed by Brown in the absorption spectrum of bromine vapour are represented by the sign ○ and those by the author in the emission spectrum of the flame by the sign + for simplicity.

(ii) $U(r)$-curves of Br_2

In order to make clear the mechanism of the emission of the bromine bands let us draw the $U(r)$-curves of the bromine molecule. The formula to express the potential energy U in a diatomic molecule has been given by Morse[9] thus:

$$U = E_e + D_e[1 - e^{-a(r-r_e)}]^2 \text{cm}^{-1},$$
$$a = \sqrt{8\pi^2 c x_e \omega_e \mu / h} \text{ cm}^{-1}. \qquad (3)$$

The vibrational energy $G(v)$ of a diatomic molecule whose vibrational quantum number is v is expressed by

$$G(v) = \omega_e\left(v + \frac{1}{2}\right) - x_e\omega_e\left(v + \frac{1}{2}\right)^2 + y_e\omega_e\left(v + \frac{1}{2}\right)^3 - \cdots \text{cm}^{-1}, \qquad (4)$$

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[9] W. Jevons, "*Report on Band-Spectra of Diatomic Molecules*," 1932.

where $y_e\omega_e$ is so small that the third term in the right side can be neglected when v is not so large[9]. E_e, D_e, ω_e, $x_e\omega_e$, r_e and a in these formulae are given in Table V.

Table V.

Molecular Constants of the Excited and the Normal States of the Bromine Molecule[10].

Constants	E_e	D		D_e	ω_e	$x_e\omega_e$	r_e	a
Units	cm^{-1}	volt	kcal	cm^{-1}	cm^{-1}	cm^{-1}	10^{-8}cm	10^{8}cm^{-1}
$0u^+$-state	15910.5	0.462	10.65	3827.3	165.39	1.59	2.65	1.947
$^1\Sigma g^+$-state	—	1.961	45.20	16057.5	323.86	1.15	2.28	1.655

The molecular constants in Table V have been adopted from Jevons' Report[11]. The $U(r)$-curves of the bromine molecule obtained by equation (3) is shown in Fig. 2, where the potential energy U (cm^{-1}) is taken as the ordinate and the internuclear distance r (cm) as the abscissa. The upper curve indicates the excited state and the lower one the normal state. The calculated vibrational levels are shown by horizontal lines in the figure. The arrows downwards indicate the processes of the transition for the emission bands of bromine in the flame.

The wave lengths of the emission bands starting from the vibrational states such as $v' < 5$ are, from Franck-Condon's principle, so long that they go beyond the sensitive range of the photographic plates used, and from this reason they have not been observed in practice. From Table III it is apparent that the intensities of the emission bands belonging to $v' > 15$ are very small. It follows, therefore, that the excited bromine molecules at the $0u^+$ state in the flame are, in the main, in such vibrational states as $v' = 15 \sim 0$.

[III] Chemical Reaction Mechanism.

(i) Mechanism of the emission bands of the flame

It has been clarified in the preceding section that in the reaction system of the combustion of bromine in hydrogen there must be formed the bromine molecules which have been excited to the $0u^+$ state. These molecules will be written as Br_2^* hereafter. Let us consider how Br_2^* is formed in the chemical reaction between bromine and hydrogen from the standpoint of the chemical reaction kinetics.

(1) How much excitation energy is required in the formation of the Br_2^*? The inner energy of a diatomic molecule contains, in general, electronic, vibra-

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[10] In this Table $D = D_e - G(0)$, where $G(0)$ is the vibrational energy at the absolute zero temperature.

[11] W. Jevons, "*Report on Band-Spectra of Diatomic Molecules*," 1932, p. 280.

tional and rotational energies, of which the quantum of the rotational energy is so small as to be neglected here.

According to Jevons[11], the electronic energy E_{mol} required to excite the bromine molecule from the $^1\Sigma_g^+$ state to the Ou^+ state is 45,000 cal. ($\nu^{(0,0)}=15831\text{cm}^{-1}$). Let Ev' and Ev'' represent the vibrational energies of the molecule in the excited and the normal states respectively, then the required excitation energy W is expressed thus:

$$W=E_{mol}+Ev'-Ev''. \qquad (5)$$

The vibrational energies Ev' and Ev'' can be calculated by formula (4), using the molecular constants given in Table V[12].

(2) The origin of the excitation energy W should be brought forth from the chemical reaction heat Q. If so, the amount of the reaction heat has to be enough for the excitation energy.

It has been admitted by many experimental results that the reaction:

$$Br_2+H_2=2HBr+24{,}300\text{cal.} \qquad (6)$$

proceeds according to the following reaction mechanism[13]:

$$Br_2=2Br-45{,}200\text{cal.}, \qquad (7)$$

$$Br+H_2=HBr+H-16{,}200\text{cal.}, \qquad (8)$$

and

$$H+Br_2=HBr+Br+40{,}500\text{cal.} \qquad (9)$$

The bromine atoms formed in the primary reaction (7) bring forth successively the secondary reactions (8) and (9).

In the reaction system at higher temperatures such as the flame, it can be considered that the alternate repetition of the reactions (8) and (9), namely chain reactions, may take place. In the chain reactions the reaction (9) is only an exothermic one. It follows, therefore, that the excitation energy W must have originated from the reaction heat produced in (9). Then, is the reaction heat $Q=$ 40,500cal. of reaction (9) really sufficient for W?

a) If $Ev'=0$ in equation (5), then

$$W(0)=E_{mol}-Ev'', \qquad (10)$$

where $W(0)$ represents the energy required to excite Br_2 to the lowest vibrational state of Br_2^*. If the reaction heat Q is considered to be not smaller than $W(0)$,

$$Q\geqq W(0)=E_{mol}-Ev'', \qquad (11)$$

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[12] $Ev=hc\cdot G(v)$ erg., and between the units of energy there holds the following relation: 1 volt $=8106\text{cm}^{-1}=23{,}055\text{cal}=1.58\times10^{-12}$erg/molecule.

[13] K. F. Bonhoeffer u. P. Harteck, „*Grundlagen der Photochemie*,“ 1933, S. 233.

and, therfore,

$$Ev''\geqq E_{mol}-Q. \qquad (12)$$

Substituting $E_{mol}=45{,}000$cal. in (12), we have $Ev''\geqq 4{,}500$cal. which corresponds to the energy of the vibrational state of Br_2 whose vibrational quantum number v'' is 5. This shows that the Br_2 molecule which has been in the vibrational states higher than $v''=5$ may be excited to become Br_2^*. And in fact the presence of the molecules in such vibrational states higher than $v''=5$ is evident from the appearance of the absorption bands belonging to these states in the absorption spectrum of bromine vapour (Table IV). With rising temperature the molecules can advance to higher vibrational states by gaining vibrational energies, and so it is apparent that in the case of higher temperatures such as the flame a number of molecules in the states higher than $v''=5$ exist.

b) The excitation energy required to excite the molecule to the vibrational state $v'=15$ in the excited state is

$$W(15)=E_{mol}+Ev'-Ev'', \qquad (10')$$

where $Ev'=6{,}000$cal. for $v'=15$ from calculation. When we assume that the mean collision energy ($E_{kin}=5{,}000$cal.) possessed at the temperature of the flame participates in the excitation, we have

$$Q+E_{kin}\geqq E_{mol}+Ev'-Ev'', \qquad \therefore\ Ev''\geqq 5{,}500\text{cal.}$$

The vibrational state of $Ev''=5{,}500$cal. corresponds to the vibrational quantum number $v''=6$. Therefore, the Br_2 molecules in the vibrational states such as $v''\geqq 6$ will be excited to the vibrational state such as $v'=15$ in the Ou^+ state. The excitation of the bromine molecule in the flame can be explained from the reaction energy $Q=40{,}500$cal. generated in reaction (9)[14].

(3) As at the temperature of the flame (about 800°K) the mean kinetic energy of molecules is only 2~3 kcal., it can not be considered that the whole of the reaction heat 40.5 kcal. turns into the translational energy of the molecules generated, i.e. HBr and Br, but that almost the whole becomes the inner energy of those molecules. HBr or Br, however, has none of the electronic excited state in the neighbourhood of the energy level as 40.5 kcal. Accordingly, if the rotational energy of HBr is not taken into cosideration, Q is to be accumulated as

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[14] In the chemical reaction system of the flame H- and Br-atoms have of course been generated, but in the spectrum of the flame neither line spectra due to these atoms nor many-lined spectrum belonging to the H_2 molecule could be found. This may be ascribed to the fact that the excitation energy W of these atoms or molecules is far higher than the reaction heat Q of reaction (9). For the appearance of the emission spectra of H_2, H and Br in the observable range they require at least the following energies: H_2, 318 kcal.; H (Balmer α), 276 kcal.; Br, 180 kcal.

the vibrational energy of HBr immediately after reaction (9). Let HBr* represent the hydrogen bromide molecule possessing so much vibrational energy. The calculation made[15] shows that it is possible for the normal hydrogen bromide molecule to have the energy 40.5 kcal. if it is in the vibrational state whose vibrational quantum number v'' is 6. In the studies of the infra-red absorption spectra of hydrogen bromide the vibrational states such as $v''=2, 1, 0$ in the $^1\Sigma$ state have been observed and in the near future the presence of such a vibrational state as $v''=6$ will be ascertained.

(4) Let us assume that the mean life of HBr* is considerably long and its vibrational energy is scarcely lost before collision. Then we can imagine that in the collision of HBr* with Br_2 the excess energy of HBr* may be transferred to the colliding Br_2 molecule, and the latter may be excited, thus:

$$Br_2(^1\Sigma_g^+) + HBr^* = Br_2^*(Ou^+) + HBr. \qquad (13)$$

Br_2^* formed in (13) will again return to its normal state emitting the band spectrum in the flame, thus:

$$Br_2^*(Ou^+) = Br_2(^1\Sigma_g^+) + h\bar{\nu}, \qquad (14)$$

where $\bar{\nu}$ is the frequency of the emission band.

In short, the mechanism of the emission of the band spectrum is explained as follows: the reaction energy Q produced in reaction (9) is accumulated in HBr as the vibrational energy immediately after the reaction, and when it collides with Br_2, this molecule may be excited. The excited Br_2 molecule presents the band emission while it returns to its normal state. As the energy of the spectrum in this case originates from the chemical reaction between bromine and hydrogen, the emission of the band spectrum of the flame can be regarded as chemiluminescence.

(ii) Branching mechanism of the chain reaction

It has been admitted that a combustion or explosion reaction has a mechanism of a branching chain reaction. Let us consider the branching mechanism of the chain in the combustion of bromine and hydrogen.

In Table V the dissociation energy of Br_2 is 45.2 kcal., which is approximately equal to its excitation energy. Therefore, when HBr_2^* collides with Br_2, there occurs not only the excitation (13) but also the decomposition of Br_2:

$$Br_2(^1\Sigma_g^+) + HBr^* = 2Br + HBr. \qquad (15)$$

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15) The calculation was done according to formula (4) by applying the molecular constants $\omega_e = 2647\text{cm}^{-1}$ and $x_e\omega_e = 44\text{cm}^{-1}$ of $HBr(^1\Sigma)$.

The Br atom thus generated becomes the origin of a new chain reaction, and thus the chain branches.

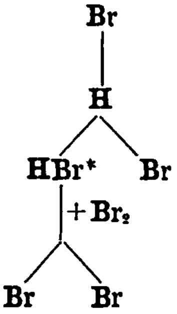
Other ways of branching of the chain reaction may also be considered. For example, (A) Br_2^* has the excess energy just sufficient for the dissociation energy of the normal Br_2 molecule as its excitation energy. Therefore, if Br_2^* collides with Br_2, according to the resonance of energies the latter decomposes thus:

$$Br_2(^1\Sigma_g^+) + Br_2^*(Ou^+) = 2Br + Br_2(^1\Sigma_g^+). \qquad (16)$$

(B) The dissociation heat of Br_2^* being 10.7kcal. as seen in Table V, it is far more unstable than the normal molecule, and apt to decompose even by simple collision, which has been confirmed by W. Jost[16] in his study of the photochemical reaction between bromine and hydrogen.

In these ways, the chain reaction branches so frequently that the reaction velocity increases very rapidly and either explosion or combustion occurs. As the concentration of Br_2^* is extremely low compared with that of Br_2, it seems more probable that the chain reaction branches according to the scheme as (8)—(9)—(15), which is shown in Fig. 3.

Fig. 3.
Schematic Expression of the Branching of the Br_2-H_2-Chain Reaction.



Which of the two reactions, (13) or (15), has larger probability to take place can not be easily discussed here. If we assume, however, that both reactions, (13) and (15), proceed at the same time, it is considered that the former explains the mechanism of the band emission observed in the flame and the latter that of the branching of the chain reaction.

Summary.

1) In the study of the emission spectrum of the flame of bromine burning in hydrogen, about 43 emission bands have been found in the range between $\lambda\lambda$ 6875 and 5600 Å, and the wave length of the band heads measured.

2) In comparison of the emission band of the flame with the absorption band of bromine vapour, both wave lengths have been quite in good agreement, and so it has been clarified that the emission band in the flame belongs to the bromine molecule and that its electron transition is thus: $Ou^+ \rightarrow {}^1\Sigma_g^+$.

3) From the results obtained by band-head analysis the vibrational quantum

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16) W. Jost, *Z. physik. Chem.*, 134, 92 (1928); [B], 3, 95 (1929).

numbers belonging to the emission bands of bromine have been determined as follows:

$$v'=5,\ 6,\ 7,\ \ldots\ldots,\ 21;\qquad v''=1,\ 2,\ 3,\ \ldots\ldots,\ 7.$$

It has been assured that the excited bromine molecules in the Ou^+ state are generated in the chemical reaction system of the flame.

4) The process of the band emission has been explained by the $U(r)$-curve of Br_2 drawn by Morse's function.

5) The mechanism of the generation of the excited bromine molecules during the combustion reaction has been discussed from the standpoint of the mechanism of chemical reaction and it has been concluded that the band emission of the flame is a sort of chemiluminescence.

6) The mechanism of the branching of the chain reaction in the case of the combustion reaction has been proposed thus:

(8) $Br+H_2=HBr+H$, (14) $Br_2^*=Br_2+h\bar{\nu}$,

(9') $H+Br_2=HBr^*+Br$, (15) $HBr^*+Br_2=HBr+2Br$,

(13) $HBr^*+Br_2=HBr+Br_2^*$, (16) $Br_2^*+Br_2=Br_2+2Br$.

of these, (8)—(9')—(13)—(14) represents the mechanism of the band emission and (8)—(9')—(15)— or (8)—(9')—(13)—(16)— the mechanism of the branching of the chain reaction.

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