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

By TETSUZÔ KITAGAWA.

Introduction.

An emission spectrum of a flame of burning gases is not similar to that of the black body radiation; the latter is a continuous spectrum expressed by the Wien-Planck radiation formula, while the former shows frequently a band spectrum, continuous spectrum or line spectrum, which is to be attributed to the electronic excited state of molecules or atoms. It may be supposed that the excitation of molecules or atoms in the flame is caused by the energy evolved in the gaseous reaction. If we could detect the carriers of the spectrum and moreover make the mechanism of the excitation clear, we might be able to explain the mechanisms of some combustion reactions of various gases.

The author took up the reaction between hydrogen and chlorine, that is, "Chlorknallgas" reaction, and studied spectroscopically the emission of the flame of chlorine burning in the atmosphere of hydrogen. Urey and Bates[1] had already found in the flame of chlorine and hydrogen a continuous spectrum extending from the visible part to the ultraviolet, which was explained by them as a recombination spectrum of chlorine atoms. Now the author has found the appearance of some bands in the region from λλ6500 to 5590 Å, which was analysed as the vibrational scheme. In this paper the mechanism of the emission of these bands is mainly discussed, and besides an explanation of the mechanism of the explosion of the "Chlorknallgas" is given.

(I) The Emission Spectrum of the Flame.

(1) Apparatus.

The main part of the apparatus is shown in Fig. 1 (a). F is a quartz window. In order to burn the flame the jet C with D was removed out of the bulb, and hydrogen was burned in the air at the mouth B. Then, the jet was inserted through the flame into B maintaining the continuous flow of chlorine. Thus the hydrogen-chlorine-flame was made at the jet C and the hydrogen-flame in the air was extinguished by shutting the ground mouth D. The jet C was made of quartz. Grease which was used in the paths of chlorine was previously saturated with it.

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*This paper is the translation of the same article in *Rev. Phys. Chem. Japan*, 8, 71 (1934).

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

A glass prism spectrograph with three 60° angle prisms was designed and constructed for use. Its dispersion was 12 Å/mm at λ4500 Å and 45 Å/mm at λ5900 Å. Iron arc spectrum was used as the reference and Ilford Special Rapid Panchromatic Plates were used throughout the experiments.

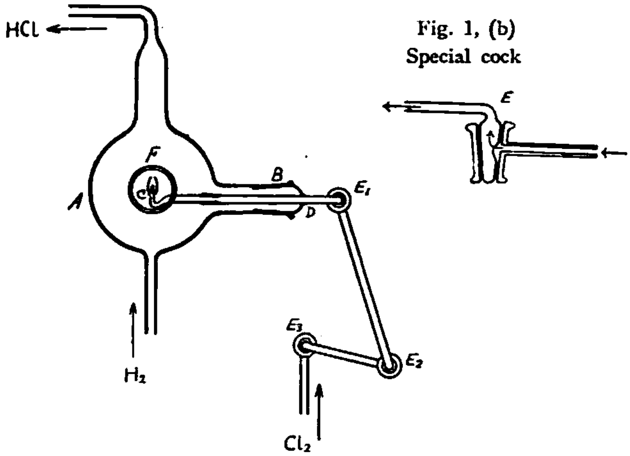

Fig. 1, (a)
Main part of the apparatus

Fig. 1, (b)
Special cock

(2) **Temperature of the flame.**

The temperature of the flame was measured by means of a thermoelement with platinum-platinum rhodium alloy, which indicated the temperature of about 900°C. But there was some reason to believe that the temperature was somewhat higher than this.

(3) **Emission spectrum of the flame.**

The flame appeared pale, a little reddish bordered. The photograph of the flame is shown in Plate I. When the emission spectrum of the flame was taken with a small quartz spectrograph (Zeiss), it was a continuous spectrum extending from the red end to the ultraviolet region up to λ2760 Å, which had been already observed by Urey and Bates.[1)]

The emission spectrum of the flame in the visible region was photographed with the above-mentioned glass spectrograph and several emission bands were found between $\lambda\lambda$6500 and 5590 Å, which had not yet been detected. The time of exposure was about 9 hours. The band spectrum is shown in Plate II (2), which has a simple structure and all the bands shade to the red. Eighteen vibrational bands were measured, and the wave

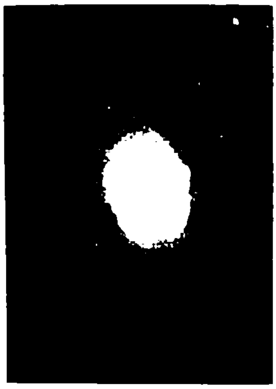

Plate I
Chlorine-hydrogen-flame
(Enlarged × 2)

lengths and wave numbers of these band-heads are shown in Table 1.

Table 1.

Emission bands of the chlorine-hydrogen-flame.

No.	λ, Å	ν, cm⁻¹	Int.	No.	λ, Å	ν, cm⁻¹	Int.
1	5590	17883	1	10	5942	16825	5
2	5630	17757	1	11	6003	16655	5
3	5669	17636	2	12	6073	16463	4
4	5716	17491	3	13	6134	16297	3
5	5761	17352	4	14	6201	16121	2
6	5821	17175	4	15	6267	15952	1
7	5842	17113	4	16	6344	15758	1
8	5882	16997	5	17	6419	15574	1
9	5898	16951	5	18	6501	15378	0

(4) Carriers of the emission bands.

From the simple structure of these bands, it is very probable that the carrier of the bands is a diatomic molecule. The diatomic molecules in the flame are hydrogen, chlorine, and hydrogen chloride. The molecular spectrum of hydrogen is known as the "many-lined spectrum" and does not exhibit an ordinary band-form. Hydrogen chloride has an absorption only in the ultraviolet region below λ2300 Å and nothing in the visible part. The carrier of the bands, therefore, will be chlorine. In the following experiments the absorption spectrum of chlorine was photographed for the purpose of the comparison.

(II) Absorption Spectra of Chlorine at High Temperatures.

(1) Apparatus.

A quartz tube with a diameter of 1.5 cm and a length of 120 cm was used as the absorption tube, the two ends of which were blown into bulbs in place of transparent windows. Chlorine gas of a pressure of about 60 cm-Hg at ordinary temperatures was fused into the tube. The tube was wound with nichrome wire (B. S. No. 18.), covered outside with asbestos and placed in the wall of "Isolite" brocks. The absorption tube was heated by means of the electric current through the nichrome wire and the temperature was measured with a thermoelement placed near the tube. A tungsten lump (200 Watts) was used as the light source.

(2) Absorption spectra at various temperatures.

The absorption spectra at various temperatures were photographed as shown in Plate III, No. 1–7 (at 22°, 285°, 360°, 560°, 650°, 730° and 810°C resp.). The time of exposure was 2 minutes. At the ordinary temperatures chlorine showed absorption bands merely in the region between λλ5300–4785 Å; and when the temperature was raised, many new absorption bands appeared and the spectrum extended itself more and more to the red region. The chlorine gas at high temperatures appeared reddish.

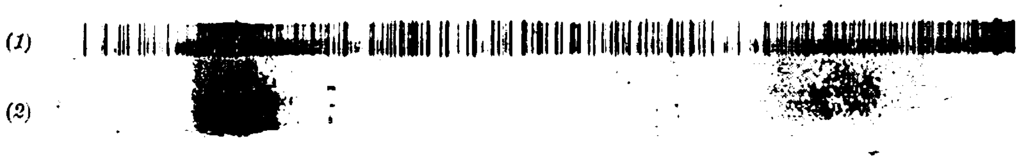

Plate II. Emission bands in the chlorine-hydrogen flame.
Upper (*1*), Fe-arc spectrum; Lower (*2*), Flame spectrum.

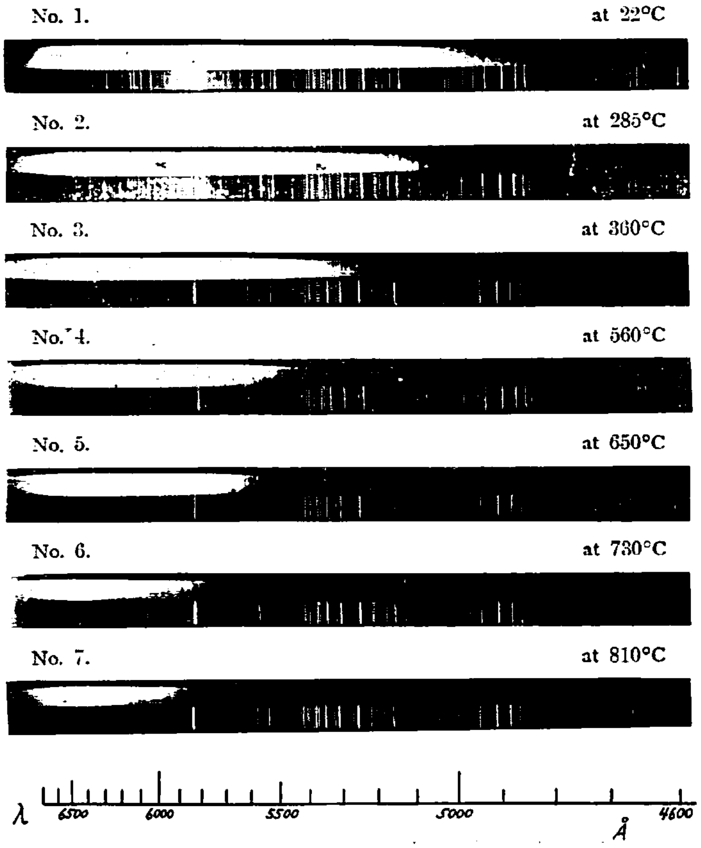

Plate III, No. 1-7.
Absorption bands of chlorine at various temperatures.
{Upper, Chlorine absorption spectra.
{Lower, Iron arc spectra (ref.).

The effect of temperature upon the region of the absorption bands is explained by means of the Franck-Condon principle.[3)4)] Fig. 2 shows the U (r)-curves of the chlorine molecule drawn by the Morse function[2)] using the data taken from Jevons' Report[3)]. In Fig. 2 the potential energy, U, is taken as ordinate, and the distance, r, between two nuclei as abscissa. The lower curve represents the normal state (${}^1\Sigma_g^+$) and the upper one the excited state (O_u^+) of the chlorine molecule. v'' and v' represent the vibrational quantum numbers for the normal and the excited molecular states respectively. At low temperatures the chlorine molecules for the most part vibrate in some low vibrational levels of $v''=0$, 1 or 2 of the lower U (r)-curve, while as the temperature rises and the molecules gain more vibrational energies, those in the higher vibrational states of $v''=3$, 4, 5, 6,............ increase. According to the Franck-Condon principle[4)] these molecules absorb the bands of longer wave lengths than before as shown in Fig. 2.

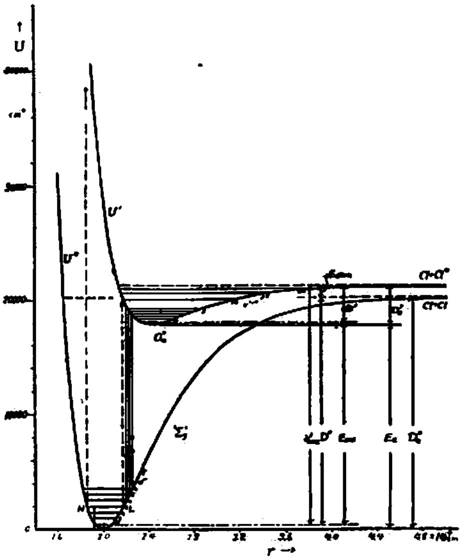

Fig. 2. U (r)c-urves of the Cl_2-molecule with vibrational levels.

(3) Comparison of the emission bands in the flame with the absorption bands of chlorine.

The absorption band-heads of chlorine at high temperatures were measured between λλ6500 and 5380 Å as given in Table 2. These bands also shade to the red. In comparison of Table 2 with Table 1, it is found that many bands in the former correspond to those in the latter. When the corresponding bands are arranged side by side (Table 3), the identity of these two band-systems will be clear, which is further supported by the fact that both the band-systems shade to the red. The carrier of the emission bands, therefore, is decidedly the chlorine molecules in the flame.

According to Mulliken[5)] the emission band spectrum in the flame is, then, due to the transition from the excited state O_u^+ to the normal state ${}^1\Sigma_g^+$ of the chlorine molecule, namely $O_u^+ \rightarrow {}^1\Sigma_g^+$. Therefore, a large number of the excited

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2) P. M. Morse, *Phys. Rev.*, **34**, 57 (1929).
3) W. Jevons, "*Report on Band-Spectra of Diatomic Molecules*", 1932.
4) J. Franck, *Trans. Farad. Soc.*, **21**, 536 (1925); E. U. Condon, Phys. Rev., **28**, 1182 (1926).
5) R. S. Mulliken, *Rev. Mod. Phys.*, **4**, 1 (1932).

Table 2.
Absorption bands of chlorine at high temperatures.

No.	λ, Å	ν, cm^{-1}	No.	λ, Å	ν, cm^{-1}
1	5384.6	18566	16	5786.9	17276
2	5427.7	18419	17	5819.3	17180
3	5463.2	18299	18	5845.5	17103
4	5475.6	18258	19	5878.1	17008
5	5502.2	18170	20	5898.5	16949
6	5521.6	18106	21	5945.1	16816
7	5546.1	18026	22	6008.8	16638
8	5590.3	17883	23	6064.8	16484
9	5625.8	17770	24	6133.1	16300
10	5646.0	17707	25	6204.5	16113
11	5669.0	17635	26	6265.1	15957
12	5680.7	17599	27	6344.6	15757
13	5702.1	17533	28	6429.4	15550
14	5713.4	17498	29	6511.9	15352
15	5762.2	17350			

Table 3.
Comparison of the absorption bands of chlorine with the emission bands of the flame.

No.	Chlorine-bands cm^{-1}	Flame-bands cm^{-1}	Diff. cm^{-1}	Calculated wave numbers cm^{-1}
1	17883	17883	0	17886.2
2	17770	17757	−13	17766.0
3	17707			
4	17635	17636	1	17635.0
5	17599			
6	17533			
7	17498	17491	− 7	17493.1
8	17350	17352	2	17340.4
9	17276			
10	17180	17175	− 5	17176.8
11	17103	17113	10	17110.1
12	17008	16997	−11	17002.4
13	16949	16951	2	16968.2
14	16816	16825	9	16815.5
15	16638	16655	17	16651.9
16	16484	16463	−21	16477.5
17	16300	16297	− 3	16298.6
18	16113	16121	8	16135.0
19	15957	15952	− 5	15960.6
20	15757	15758	1	15775.4
21	15550	15574	24	15579.3
22	15352	15378	26	15372.4

chlorine molecules (in the O_u^+-state), which will be later on written as Cl_2^*, must be generated by the chemical reaction in the flame.

(III) Decision of the Quantum Numbers v′ and v″ from the Band Analysis.

The absorption band-heads in Table 2 are analysed and the results are shown in Table 4. Some of the bands framed in Table 4 come out as the emission bands in the hydrogen-chlorine-flame.

Table 4.

Band-analysis.

v′ \ v″	2	3	4	5	6
5			16638		
6		17350 (17352.1)	16816 (16813.1)	16300	15757
7	18106 (18088.8)	17533 (17536.5)	17008 (16994.1)	16484	15957
8	18258 (18261.8)	17707 (17707.0)	17180 (17166.8)	16638	16113
9	18419 (18417.9)	17883 (17866.7)	17350 (17338.5)	16816	16300
10	18566 (18578.7)	18026 (18024.5)	17498 (17496.0)	16949	
11		18170 (18167.0)	17635 (17637.6)	17103	
12		18299 (18295.9)	17770 (17765.1)		
13		18419 (18414.5)	17383		

The analysis of the absorption bands of chlorine has been carried out by Elliott[6] using the data given by Nakamura[7] and Kuhn[8]. The simplified expression for this result is shown in Table 5 and the band-heads measured by them are shown by the sign ○. In Table 4 the wave numbers of band-heads given by Nakamura are shown in parentheses and they are in good agreement with those of the author. Comparing these two series of data, the author was able to decide the vibrational quantum numbers of the emission bands as shown by the

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[6] A. Elliott, *Proc. Roy. Soc.*, A, 123, 629 (1929); 127, 638 (1930).

[7] G. Nakamura, *Mem. Coll. Sci. Kyôto Imp. Univ.* A, 9, 353 (1926).

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

Table 5.
Simplified expression of the analysis of absorption bands of chlorine.

v' v''	0	1	2	3	4	5	6
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	○	○					
25	○						
26	○						
27	○						

○ Absorption bands observed by Nakamura and Kuhn.
△ Emission bands in the H_2-Cl_2-flame observed by the author.

sign △ in Table 5. The vibrational quantum numbers of the emission bands are thus determined as $v'=5-13$, and $v''=4$, 5 and 6.

The wave numbers of the chlorine bands may be calculated by the following formula given by Elliott:6)

$$\nu=17657.7+(255.7v'-5.42v'^2)-(560.9v''-4.0v''^2).$$

Given the values of $v'=5-13$ and $v''=4-6$, the wave numbers of the emission band-heads are obtained, which coincide well with the observed values as shown in the last column of Table 3.

The initial quantum numbers v' of the emission bands were 5 to 13, and the bands with $v'<5$ were not observed, but it is probable from the Franck-Condon theory that the wave lengths of these bands became so long that they could not be detected in the sensible region of the panchromatic plates used. The excited chlorine molecules Cl_2^* in the flame, therefore, may exist mainly in the vibrational levels lower than with $v'=13$.

(IV) Mechanism of the Formation of the Excited Chlorine Molecules.

It has now been clarified that in the reaction in the flame of chlorine and hydrogen a considerable amount of the excited chlorine molecules, Cl_2^*, is formed, which must be excited by the energy produced in the chemical reaction. The mechanism of the excitation of the chlorine molecules will be considered next.

(a) The mechanism of the photochemical change of chlorine and hydrogen[9] is

$$Cl_2+h\nu=Cl+Cl^*, \qquad (1)$$

$$Cl+H_2=HCl+H+\sim 0\ \text{kcal}, \qquad (2)$$

$$H+Cl_2=HCl+Cl+45\ \text{kcal}, \qquad (3) \quad \text{etc.}$$

The normal chlorine molecule absorbs a light quantum and dissociates itself into two atoms. The chlorine atoms thus formed induce the chain reactions, (2), (3) and etc.[10]

In general an explosion or combustion reaction, which proceeds very swiftly, contains, as a rule, this kind of chain reactions. The heat of reaction in (2) is about zero, but in (3) the heat of reaction of 45 kcal is generated, by means of which the chlorine molecule must be excited to the O_u^+-state.

The excitation energy of the chlorine molecule depends upon the vibrational state of the normal molecule, and if the normal molecules exist at least in the vibrational states of $v''=4$ or 5, they are just able to be excited by the reaction heat of 45 kcal added with the translational energy possessed by them at the temperature of the flame. The absorption spectra of chlorine at high temperatures (Plate III) show that the molecules with $v''=4, 5, 6, \ldots\ldots$ exist actually at those temperatures.

(b) In what course, then, is a chlorine molecule excited by the heat of reaction? Though it was assumed by Semenoff[11] that the reaction heat of reaction (3) was equally shared by the products Cl and HCl (23 kcal each) in the form of the translational energy, the mean kinetic energy of molecules at the temperature of the flame is only about 4 kcal from calculation, and consequently it is impossible that a molecule or atom possesses such large energy as 23 kcal given by Semenoff for translational form at that temperature.

Thus the heat of reaction must be stored as the inner energy of the molecule, namely as electronic, vibrational, or rotational energy. From spectroscopic considerations it is inconceivable that HCl or Cl reserves such an amount

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[9] C. N. Hinshelwood, "*The Kinetics of Chemical Change in Gaseous Systems*", 1933.

[10] It has been discussed by Rollefson and others whether the excited chlorine atom has a larger activity than the normal or not, but the reliable conclusion has not yet been obtained. It is assumed here that the excited chlorine atom reacts as actively as the normal one, because the excited state has the excessive energy of merely 2.5 kcal to the normal.

[11] N. Semenoff, *Z. physik. Chem.* B, 2, 161 (1929); "*Chemical Kinetics and Chain Reactions*," 1935.

of energy as 45 kcal for the electronic energy. Moreover, its rotational energy is very small. And the whole of the energy should be stored in the HCl molecule as the vibrational energy.

If we assume that the normal molecule of HCl possesses 45 kcal as its vibrational energy, it is found by calculation[12] that the molecule exists in the vibrational states with the vibrational quantum numbers of v=5 or 6. As the vibrational states of v=0, 1, 2, 3 and 4 of the HCl molecule[13] have been well examined in the studies of the infra-red absorption spectrum of the HCl gas and their existence is certain, the existence of the states with v=5 or 6 will also be assured. When the HCl molecule possessing such large vibrational energy is expressed by HCl*, reaction (3) is replaced by

$$H+Cl_2=HCl^*+Cl. \qquad (3')$$

The molecule HCl* has just the amount of the vibrational energy enough to excite a normal chlorine molecule to the electronic excited state (O_u^+), and when HCl* collides with the normal chlorine molecule, the exchange of energy may take place very easily between them by the resonance phenomenon of energies, that is,

$$Cl_2+HCl^*=Cl_2^*(O_u^+)+HCl. \qquad (4)$$

The three body collision process:

$$H+Cl_2+Cl_2=HCl+Cl+Cl_2^*(O_u^+) \qquad (3'')$$

may also be expected to occur, but the probability of the occurrence of this reaction will be very small in comparison with the former.

(c) The excited chlorine molecules Cl_2^*, which are mainly formed by the collisions between the normal Cl_2 and the active HCl* in reaction (4), return to the normal state emitting the emission bands as shown in Plate II, as

$$Cl_2^*(O_u^+)=Cl_2(^1\Sigma_g^+)+h\nu. \qquad (5)$$

On the contrary to our anticipation any other lines such as those of the Balmer series of the hydrogen atom could not be observed in the emission spectrum of the flame. The reason of this can be understood from the facts that for the excitation energy of the Balmer H_α-line at least 276 kcal is indispensable, and that the reaction heat of 45 kcal is far insufficient for it, although hydrogen atoms might be produced in the flame.

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[12] The vibrational energy of the HCl molecule can be calculated by the formula: $G(v)=\omega_e(v+1/2)-x_e\omega_e(v+1/2)^2$, where v is the vibrational quantum number. The values of the constants are given for HCl as $\omega_e=2989.68$ cm^{-1} and $x_e\omega_e=51.90$ cm^{-1}, where 353 cm^{-1} corresponds to about 1 kcal.

[13] Schaefer and Matossi, "*Das ultrarote Spektrum*," 1930; G. Herzberg and J. W. T. Spinks, *Z. Physik*, **89**, 474 (1934); A. P. Cleaves and C. W. Edwards, *Phys. Rev.*, **48**, 850 (1935).

(V) On the Mechanism of the Explosion Reaction of Hydrogen and Chlorine.

(a) Postulation of a new branching chain reaction mechanism.

Now, we will consider how the Cl_2^* molecules play as the intermediate product in the inflammable or explosive reaction between chlorine and hydrogen. The chlorine atom is an important intermediate product of the reaction. For the dissociation of the normal chlorine molecule into two atoms about 57 kcal is required, while for that of the excited chlorine molecule is merely about 9 kcal as follows:

$$Cl_2^*(O_u^+) = Cl(^2P_{3/2}) + Cl^*(^2P_{1/2}).$$

This is also understood from Fig. 2, in which the minimum of the upper curve is very slight, and if the Cl_2^* molecule has some vibrational energies, it will be easily dissociated into atoms when another molecule M collides with it, that is,

$$Cl_2^* + M = Cl + Cl^* + M. \qquad (6)$$

In photochemical experiments of the reaction between chlorine and hydrogen Hertel[14] has found that the reaction took place by the dissociation of the excited chlorine molecule by the impact with another molecule.

When the reactions which take place in the flame of chlorine and hydrogen are arranged in due succession, a new chain reaction mechanism is settled:

$$Cl + H_2 = HCl + H, \qquad (2)$$

$$H + Cl_2 = HCl^* + Cl, \qquad (3')$$

$$HCl^* + Cl_2 = HCl + Cl_2^*, \qquad (4)$$

$$Cl_2^* = Cl_2 + h\nu, \qquad (5)$$

$$Cl_2^* + M = Cl + Cl^* + M. \qquad (6)$$

The chain reaction of (2) and (3′) is what is called Nernst's chain, while the active molecule HCl^* produced in (3′) induces the following new reactions (4), (5) and (6), and in the last stage two chlorine atoms are produced. These atoms become again the nuclei of two new chains, and here the chain reaction branches. The branching scheme of the chain reaction is shown diagrammatically in Fig. 3. The reaction velocity is thus violently accelarated by the branching of chains and an explosion occurs.

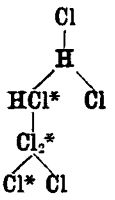

Fig. 3. Branching scheme of the H_2-Cl_2 chain reactions.

In the reaction between chlorine and hydrogen it was assumed by Semenoff[11], that the reaction heat, 45 kcal. of reaction (3) was equally shared between the products of the reaction 23 kcal each, and that

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[14] E. Hertel, *Z. physik. Chem.* B, 14, 443 (1931).

a chlorine molecule possessing an energy of about 34 kcal collided with the product the former was dissociated into atoms and the chain branched. As already stated, however, the heat of reaction of (3) could not be transferred to the products as their translational energy and the chlorine molecule having such a large amount of energy as 34 kcal would not be likely to exist. Thus it is very probable that the excited chlorine molecule Cl_2^* as an intermediate product of the explosive reaction plays a great part in the mechanism, and the above interpretation of the explosive reaction between hydrogen and chlorine seems to be more natural.

(b) Calculation of the probability of the branching of the chain reaction.

Let us calculate the probability of the branching of the chain reaction from our reaction mechanism.

(i) For the occurrence of the reaction:

$$HCl^* + Cl_2 = HCl + Cl_2^*, \qquad (4)$$

the normal chlorine molecule at least should have vibrational energy of about 6–8 kcal corresponding to the vibrational quantum numbers $v''=4-5$ as above stated. This amount of energy is put as U_1. The rate of excitation is, therefore, $k_4[Cl_2]e^{-\frac{U_1}{RT}}$, where $[Cl_2]$ is the partial pressure of chlorine and k_4 the proportional constant. On the other hand the active HCl^* may lose its energy by the radiation of vibration bands or by the collisions with other molecules M. The rate of its deactivation is accordingly $k_4'+k_4''[M]$, where k_4'' is the proportional constant and k_4' the probability of the radiation. Thus the probability α that the Cl_2 molecule is excited by one HCl^* molecule is expressed thus:

$$\alpha=\frac{k_4[Cl_2]}{k_4'+k_4''[M]}\cdot e^{-\frac{U_1}{RT}}. \qquad (A)$$

The probability of radiation of HCl^* has been calculated[15] quantum-mechanically as $k'_4=10^3\sim10^4\,sec^{-1}$, and its mean life is long enough to let the molecule give off its energy by collisions most frequently, and we can neglect k_4' against k_4'' in eq. (A). If the partial pressures $[Cl_2]$ and $[M]$ are assumed to be proportional to the total pressure, the probability α may be written as follows:

$$\alpha=C_1e^{-\frac{U_1}{RT}}, \qquad (A')$$

where C_1 is a constant.

(ii) In order that the excited chlorine molecule may decompose by the collision, it is assumed that at least it should have some vibrational energy of U_2 before the collision. Thus the rate of decomposition is $k_6e^{-\frac{U_2}{RT}}[M]$, where k_6

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[15] K. F. Bonhoeffer and P. Harteck, "*Grundlagen der Photochemie.*" 1933.

is the proportional constant. Meanwhile, the excited chlorine molecule may be deactivated by collisions without dissociation (ineffective collisions) or return to the normal state with the emission of the band spectrum (Plate II). The rate of deactivation of the excited chlorine molecule without decomposition is $k_5+k_5'[M]$, where k_5 is the probability of the emission in equation (5) and k_5' the proportional constant, under the assumption that the number of ineffective collisions is proportional to [M]. Thus the probability β that one excited molecule Cl_2^* decomposes is expressed by

$$\beta=\frac{k_6e^{-\frac{U_2}{RT}}[M]}{k_6e^{-\frac{U_2}{RT}}[M]+k_5+k_5'[M]}. \qquad \text{(B)}$$

Under pressures of explosion it may be assumed that the greater part of the excited molecules lose their energies by collisions and only a small part can emit the radiation, and the constant k_5 may be neglected compared with the others in (B). If it is assumed again that the number of collisions with decomposition is so small in comparison with the ineffective collisions, $k_6e^{-\frac{U_2}{RT}}$ may be neglected against k_5' and the probability β may be written approximately as

$$\beta=C_2\cdot e^{-\frac{U_2}{RT}}, \qquad \text{(B}_1\text{)}$$

where C_2 is a constant.

(iii) Lastly the probability of the chain branching, γ, is expressed by the product of the probabilities of the excitation of the chlorine molecule, α, and that of its decomposition, β, that is

$$\gamma=\alpha\times\beta=C_1C_2e^{-\frac{U_1+U_2}{RT}}. \qquad \text{(C)}$$

(c) Relation between the critical pressure of explosion and the temperature.

According to Semenoff's explosion theory[11] the velocity, w, of a branching chain reaction is given by $w=n_0l/(1-l\gamma)$, where n_0 is the number of the Cl atoms formed at the beginning of the reaction, l the length of the chain, and γ is the probability of branching. Thus the condition of explotion is $l\gamma=1$.

If the value of γ in equation (C) is introduced in the above condition of explosion under the assumption that the chain breaks in the gaseous phase, we get

$$l\gamma=\text{const.}\times P\times e^{-\frac{U_1+U_2}{RT}}=1,$$

or

$$\ln P=\frac{U_1+U_2}{RT}+C, \qquad \text{(D)}$$

where C is a constant and P is the critical pressure of explosion at the absolute temperature T.

The expression (D) is analogous to Semenoff's equation derived under the assumption of his secondary activation theory[11]:

$$\ln P = \frac{A}{T} + B, \qquad \text{(E)}$$

where both A and B are constants, A depending only upon the kind of gas mixtures and B upon the external conditions. We can now give the physical meaning to the constant A in equation (E) as $A = \frac{U_1 + U_2}{R}$. When the constant A is calculated using Sagulin's data[16], A becomes equal to about 5500. If we introduce the value of A into the realtion: $A = \frac{U_1 + U_2}{R}$ assuming $U_1 = 6-8$ kcal as stated before, we have $U_2 = 3-5$ kcal. This value of U_2 corresponds to the vibrational states of the excited chlorine molecule with the quantum numbers $v' = 5-8$. Thus it is seen that the molecules which have vibrational energies above those values may be decomposed by collisions. It is very interesting to mention that we have obtained a fairly reasonable result though some approximations were done in the calculation.

Summary.

1) The emission spectrum of the flame of chlorine burning in the atmosphere of hydrogen has been photographed and about eighteen emission bands found and measured in the region between λλ5590 – 6500 Å.

2) The absorption spectrum of chlorine at various temperatures to maximum 810°C in a quartz absorption tube has been photographed, and the band-heads measured between λλ5380—6500 Å.

3) In comparison of the wave numbers of the emission bands with those of the absorption bands of chlorine, the carrier of the emission bands has been ascertained to be the excited chlorine molecule in the O_u^+ state (Cl_2^*) formed in the flame.

4) The band-analysis was performed and the vibrational quantum numbers v' and v'' of the emission bands have been determined as 5—13 and 4—6 respectively.

5) The mechanism of the explosion reaction has been discussed under the assumption of the excited chlorine molecule as an intermediate product, and the relation between the critical pressure of explosion, P, and the absolute temperature, T, has been obtained: $\ln P = (U_1 + U_2)/RT + C$, where U_1 and U_2 are the least vibrational energies to branch the chain possessed by the normal and excited chlorine molecules respectively.

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The Laboratory of Physical Chemistry,
Kyoto Imperial University.

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[16] A. Sagulin, *Z. physik. Chem.* B, 1, 275 (1928).