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REACTIONS BETWEEN SODIUM VAPOUR AND VOLATILE POLYHALIDES. VELOCITIES AND LUMINESCENCES.¹

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The diffusion method devised by H. von Hartel and M. Polanyi ² (see Fig. 1) was applied to the reactions of sodium vapour with the following substances :

BCl₃, BBr₃, CCl₄, SiCl₄, SiBr₄, GeCl₄, SnCl₄ TiCl₄, PCl₃, AsCl₃, SCl₂, S₂Cl₂, COCl₂, POCl₃, CrO₂Cl₂, CS₂.

¹ An extract of this paper was given in Compt. rend, 1934, 199, 1118.

² Z. physikal. Chem. 1930, 11B, 97.

The list contains nearly all the completely chlorinated or brominated polyhalides which have a sufficient vapour pressure to be introduced at room temperature into the "diffusion apparatus." The present study is in the nature of a general survey in which the emphasis is on the determination of the sequence of reactivities and on the observation of a series of chemiluminescences which made their appearance while the reaction velocities were measured.

Experimental Procedure.

Preliminary to the study of these reactions, one of the authors (W. H.), in conjunction with Dr. Kodama and Mme. Schatunowskaja, has made an extensive re-examination of the diffusion method which is to be submitted shortly to this journal.

The following were the main results of this investigation. The distribution of the halogen compound throughout the flame region in the stationary state was determined for various velocities (v) of the "carrier gas," using different carrier gases (N_2, H_2) at different pressures, resulting in different values for the diffusion constant (δ) of the sodium vapour in the carrier



FIG. 1.—Main Features of the "Diffusion Method."—Na-vapour is carried by a flow of carrier gas into the reaction vessel, where it meets the flow of a gaseous halogen compound Hl ("halogen gas"). The reaction zone is illuminated by a sodium resonance lamp (L), the sphere of sodium vapour thus made luminescent is the "flame," the diameter D of which is measured. D is estimated through a window at O by a sighting device which is adjusted successively to the upper and to the lower edge of the "flame."

gas. It was established that conditions must be so adjusted that v/δ (v in m./sec. and δ in cm.²/sec.) should be between 5×10^{-3} and 12×10^{-2} , since at higher values the halogen compound is "swept out" of the flame region, while at lower values the back diffusion into the nozzle falsifies the results. The conclusion was also reached that the measurement should be based on flames of large size, if possible not smaller than 3.5 cm. in diameter.

Various improvements relating to the control of the inflowing "halogen gas" stream lead to a more accurate determination of the partial pressure of the halogen gas in the reaction zone. At the same time, a more reliable estimation of the flame diameter was introduced by "end on" observation with a levelling device adjustable to the edges of the flame. The method thus improved, yields relative velocity constants of about 15 per cent. accuracy for reactions requiring not less than about 50 and not more than about 5000 collisions.

Apart from these technical developments, of which full use has been made in the present work, special provisions were made for the handling of the halogen compounds, most of which are extremely sensitive to moisture, and attack tap-grease and mercury. The purchased halogen compounds were opened in vacuo and distilled into the apparatus. The flow of halogen gas was controlled by values of the membrane type (Fig. 2) and the mercury in the manometers covered with sulphuric acid or paraffin oil. Owing to these technical difficulties the capillaries, by which the flow of the halogen

gas is controlled, could be calibrated only for a few of the inorganic polyhalides. The flow of the other halogen gases was calculated on the assumption that the viscosity of the vapours does not differ appreciably. This was found to be true in a comparison carried out between CCl_4 and $SiCl_4$ as well as between a large number of halogenated organic compounds. It is believed that the error caused by the assumption of equal viscosities cannot affect the sequence of reactivities as stated below.³

The reaction rates of CCl₄, SiCl₄, BCl₃, BBr₃, TiCl₄ fall within the range stated previously for which we estimate the accuracy of the relative values to be about 15 per cent. The other compounds react so fast as to lie beyond the range of velocities for which the method can be used quantitatively; in these cases only the order of magnitude of the reaction rates could be established. As to



FIG. 2.—Rotation of the knob K moves the screw S vertically. This motion is transmitted through the metal vacuum-tight diaphragm D to the needle, which can thus be raised or lowered into the valve seating V. The cones C are used to connect the valve to the apparatus.

the sequence of values given for this group of substances, we see no reason why the sequence of any pair of values differing by more than 30 per cent. should not be correct.

Reaction Velocities.

The results listed in Table I. all refer to a reaction temperature of 270°. The partial pressure p_{Na} of sodium at the nozzle was nearly 3.10⁻³ mm.; deviations from this value were duly taken into account. The carrier gases used were H₂ and N₂ (the former for faster, the latter for slower reactions), and their pressures were varied from I mm. to 10 mm. Each reaction velocity was determined by a series of measurements on flames of different sizes; on the average five flames were measured, ranging in size from 2 cm. to 4.5 cm. The values listed in the table are interpolated for the size of 3.5 cm.

The calculation of the velocity constants is based on the formula

$$k = \frac{\left(\ln \frac{p_{\text{Na}}}{p_0} - \ln \frac{R}{r}\right)^2}{(R-r)^2} \cdot \frac{\delta}{p_{\text{HI}}} \cdot \frac{I}{T},$$

³ For a determination of the absolute values of reaction rates the distribution of the halogen gas throughout the flame has to be taken into account. The influence of this correction will be shown in the detailed communication on the improvements of the experimental method, where specific reference will once more be made to the case of CCl_4 .

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Compound.	Reaction Velocity Constant k (c.c. mole ⁻¹ sec. ⁻¹ × 10 ⁻¹¹).	Collision Number (S).	
BCl ₃	4.21	1,350	
CCl ₄	963	6 ·5	
SiCl ₄	4:03	1,570	
TiCl ₄	993	6·4	
GeCl₄	4,890	1·3	
SnCl₄	3,510	1·8	
PCl ₃	1,500	4·2	
AsCl ₃	1,470	4·3	
SCl ₂	6,340	1.0	
BCl ₃	4'71	1,350	
BBr ₃	248	25·6	
SiCl ₄	4'03	1,570	
SiBr ₄	1,450	4·4	
S2Cl2	1,760	3.6	
SCl2	6,340	1.0	
PCl3	1,500	4.2	
POCl3	2,290	2.8	
COCl ₂	856	7·4	
CrO ₂ Cl ₂	1,330	4·8	
CS.	~ .0306	207,500	

TABLE I.

where p_{Na} and p_0 are the partial pressures of sodium at the centre and at the edge of the flame respectively, p_0 being 10^{-5} mm.; R and r are the radii of the flame and the nozzle respectively, r being 0.25 cm.; δ is the diffusion constant of sodium vapour in the carrier gas, and was calculated for the prevailing conditions on the basis of earlier determinations ⁴ by which the values $\delta_{Ha} = 3.14$ and $\delta_{Na} = 0.92$ had been obtained for atmospheric pressure, and 643° K.; p_{HI} is the partial pressure of the halogen gas in the reaction chamber and T the absolute temperature. The reaction velocity constants k are in the units of c.c/.mol. sec.

The "collision numbers" (S) also listed in the table are based on a uniform collision diameter of $6.7.10^{-8}$ cm. We thus obtain the relation

$$S=\frac{6\cdot 3\times 10^{14}}{k}.$$

The molecular velocities of the halogen compounds range between 17,000 and 34,000, which are the values for $COCl_2$ and $SiBr_4$ respectively. This causes a variation in the collision no. of ± 3 per cent. which has been taken into account in the evaluation of S.

In the table we have grouped our results in the following way. The chlorides are listed in the sequence of their position in the periodic system of elements. Then the bromides $(BBr_3 \text{ and } SiBr_4)$ are shown in juxtaposition to the corresponding chlorides. The next section points out the effect of a change in valency of the atom to which the halogen is linked; finally, the values for $COCl_2$, CrO_2Cl_2 and CS_2 are given.

We note in the first part of the table that there is a considerable inertia attached to the reactions of BCl_3 and $SiCl_4$; the inertias of CCl_4 , $TiCl_4$, PCl_3 and $AsCl_3$ are noticeable; the reactions of $GeCl_4$, $SnCl_4$ and

⁴ H. von Hartel, N. Meer and M. Polanyi, Z. physik. Chem. 1932, 19B, 139.

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 SCl_2 are practically instantaneous. If we add to the data listed in the first section of the table, the fact that the reactions of sodium vapour with Cl_2 . Br_2 and I_2 are all instantaneous, we cannot fail to observe that the tendency for an inertia to be present falls off when we pass from the third and fourth groups to the higher groups of the system. The fact that the volatile halogenides of the second period (HgCl₂, CdCl₂, ZnCl₂, CuCl₂) all react instantaneously suggests that the inertia has its maximum in the middle groups of the periodic system, and falls off both towards lower and higher groups. This corresponds to the changes in bond strength of the halogen atoms which are highest for the middle groups of the periodic system.

The second part of the table illustrates the increase in reactivity caused by substituting Br for Cl; a rule repeatedly observed previously in the organic series. The ratio of the velocities of the Cl and Brcompounds is similar to that found in the organic series.

An increase in reactivity, corresponding to decreasing bond strength, is also found in the two cases where compounds corresponding to a higher valency stage can be compared with compounds of a lower valency stage : SCl_2 reacts faster than S_2Cl_2 ; POCl₃ faster than PCl₃. (The oxygen atom introduced in the latter case seems to have little effect, since COCl₂ does not react faster than CCl₄.)

A measure of bond strength most appropriate to our problem is given by the restoring forces of the bonds, as derived from Raman spectra. Table II. illustrates the parallelism of the "inertia" deter-

Compound:	Collision Number (S).	Restoring Force Constants $(f \times 10^{-5})$ between Central Atom-Hl-Atom.
CCl	6.5	2.00
SiCl₄	1,570	2.42
TiCl	6.4	2.20
GeCl ₄	1.3	
SnCl ₄	1.8	2.00
PCl _s	4.5	1.9
AsČl ₈	4.3	1.4
SbCl ₃		0.87
BiCl ₃		0.44
CH ₈ Cl	7,100*	3.12
CH ₂ Cl ₂	310*	2.94
CHČl ₃	22*	2.47
CCl ₄	2*	2.00
CH ₈ Cl	7,100*	3.12
CH ₈ Br	75*	2.61
CH ₃ I	Ĩ	2.15

TABLE II.

* These values which have been substituted for the earlier results of Hartel, Meer and Polanyi are based on new measurements of W. Heller to be published shortly.

mined by the collision number, with the restoring force constant f of the bond. Within each of the three groups, $CCl_4 \rightarrow SnCl_4$, $CH_3Cl \rightarrow CCl_4$ and $CH_3Cl \rightarrow CH_3I$ this parallelism holds equally well.

The high restoring force attributed to the linkages in $SiCl_4$ might appear unexpected; ⁵ it is, therefore, to be noted that it is borne out by

⁵ K. W. F. Kohlrausch, *Der Smekal-Raman Effekt*, 1931, page 217, expresses diffidence as to the correctness of this force constant for this reason.

the heat of formation of $SiCl_4$ which is considerably higher than that of either CCl_4 or $SnCl_4$. We have the energies

 $C_{vapour} + 4Cl = CCl_4 + 280$ kCal. Sivapour + 4Cl = SiCl_4 + 340 kCal. Snvapour + 4Cl = SnCl_4 + 310 kCal.

It seems reasonable that the force which counteracts an elongation of the halogen bond should also be responsible for the chemical inertia of such reactions which lead to the splitting up of the bond. A closer consideration of the theoretical connection of force constant and chemical inertia has been given by R. A. Ogg in conjunction with one of the authors.⁶

Reaction of CS₂ with Na-Vapour.

We found that Na-vapour reacts with CS_2 -vapour. In view of the endothermicity of the process,

$$CS_2 + Na = CS + NaS_{(vapour)}$$

the observed reaction appears to be the addition

$$CS_2 + Na = CS_2Na.$$

The fact that the reaction proceeds very slowly helps to confirm this view. The observed velocity constant k (Table I.) which was measured in the presence of 6 mm. of pentane used as carrier gas, is not too large to be accounted for by three-body collisions. Indeed, the reaction is slower than in the case of the analogous reaction between Na-vapour and O_2 to which reference is made later.

Chemiluminescences.

The chemiluminescence accompanying the reaction of sodium vapour with chlorine was discovered by Haber and Zisch.⁷ When a nitrogen stream at atmospheric pressure, carrying a slight admixture of sodium vapour, was led into chlorine a slight yellow glow appeared which was found to contain exclusively the D-line of sodium.

By the use of "highly attentuated flames" this luminescence was greatly increased in intensity, and the mechanism of its origin was elucidated.⁸ At the same time, a number of similar luminescences were discovered, accompanying the reactions of Na-vapour with the various halogens and with the volatile halogen salts of the second sub-group of the periodic system. Two examples may show the mechanism of these luminescences

$$\begin{array}{l} \operatorname{Na} + \operatorname{Cl}_{2} = \operatorname{NaCl} + \operatorname{Cl} \\ \operatorname{Cl} + \operatorname{Na}_{2} = \operatorname{NaCl}^{*} + \operatorname{Na} \\ \operatorname{NaCl}^{*} + \operatorname{Na} = \operatorname{NaCl} + \operatorname{Na} + h\nu \\ \operatorname{Na} + \operatorname{HgCl}_{2} = \operatorname{NaCl} + \operatorname{HgCl} \\ \operatorname{Na} + \operatorname{HgCl} = \operatorname{NaCl}^{*} + \operatorname{Hg} \\ \operatorname{NaCl}^{*} + \operatorname{Na} = \operatorname{NaCl} + \operatorname{Na} + h\nu \end{array} \right\}$$
 Type A.

Trans. Faraday Soc., 1935, 31, 482.
 T. Physik, 1922, 9, 302.
 H. Beutler and M. Polanyi, Z. physik. Chem., 1928, 1B, 3.

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In both cases the final process of excitation consists in a collision of the "nascent" NaCl*-molecule with an Na-atom. Such chemiluminescences can arise only if there is a reaction of Na-vapour which evolves at least 48.5 kCal. which is the molar excitation energy of the D-line.

A chemiluminescence differing fundamentally from these was observed ⁹ when highly attenuated sodium vapour was brought into reaction with SnCl₄-vapour. The luminescence has a continuous spectrum, the origin of which is supposed to be

$$\begin{array}{l} \mathrm{Na} + \mathrm{SnCl}_{4} = \mathrm{NaCl} + \mathrm{SnCl}_{3} \left(\mathrm{twice} \right) \\ \mathrm{SnCl}_{3} + \mathrm{SnCl}_{3} = \mathrm{SnCl}_{4} + \mathrm{SnCl}_{2} + \mathrm{h}_{\nu} \end{array} \right\} \\ \mathrm{Type } \mathrm{B}.$$

Since, according to this view, the luminescence arises from two particles as they undergo the process of reaction, this type (B) has been given the name of "primary chemiluminescence." The atomic mechanism which may lead to primary chemiluminescence was discussed in detail in a recent paper by R. A. Ogg and one of the authors.¹⁰ An obvious condition for the occurrence of this sort of luminescence is the presence of a heat of reaction (E) satisfying the condition

$E \geq Nh\nu_{l}$

where v_1 is the short-wave limit of the continuous spectrum emitted by the reaction.

A third type (C) of chemiluminescence, the mechanism of which is still unexplained, was discovered when CuCl₂ vapour was brought into a flame of Na + Cl_2 . Besides the yellow light belonging to the Na + Cl_2 flame, an intense green luminescence made its appearance in which the well-known CuCl-bands were recognised spectroscopically. The same luminescence also arises when $CuCl_2$ is brought into an Na + HgCl₂flame, and it was observed also when CuCl₂ was introduced into a stream of atomic hydrogen reacting with chlorine; it is distinctly observable in the gas phase when chlorine attacks metallic aluminium in the presence of $CuCl_2$ vapour.¹¹ The peculiar feature of these latter luminescences lies in the fact that although no emission of light accompanies the reaction between CuCl₂ with either Na-vapour or H-atoms or metallic aluminium, the presence of another body, such as Cl₂ or HgCl₂ reacting simultaneously with these substances gives rise to the luminescence.

The chemiluminescences newly observed in connection with the reactions of the inorganic polyhalides seem to belong partly to type A or B; another group which made its appearance only when O_2 was added to the flame, shows some similarity to type C, but may prove to represent an altogether new type.

Table III. presents the observations on chemiluminescence. With CCl₄, SiCl₄, AsCl₃ and CS₂, no luminescence was observed; accompanying the reaction of TiCl₄ there sometimes appeared a faint glow, but the existence of this luminescence could not be definitely established. Clearly visible luminescences were present in the reactions of BCl₃, BBr₃, SiBr₄, GeCl₄, SnCl₄ (as previously known), PCl₃, S₂Cl₂, SCl₂, COCl₂, POCl₃ and CrO₂Cl₂ with sodium vapour.

⁹ M. Polanyi and G. Schay, Z. Physik, 1928, 47, 814.
¹⁰ R. A. Ogg and M. Polanyi, Trans. Faraday Soc., 1935, 31, 1375.
¹¹ L. Frommer and M. Polanyi, Z. physik. Chem., 1930, 6B, 371. This paper gives only a brief account of other CuCl-luminescences than those caused by Details of the other account bar presented by Details. the reaction with aluminium. Details of the other cases have remained unpublished.

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Halogen Compound.	Observed Lumines- cence, Colour.	Estimated Intensity $(ISnCl_4 = 10).$	Probable Luminescence Type.
BCl ₃	grey	1-2	в
CCl ₄ SiCl ₄ TiCl ₄ GeCl ₄ SnCl ₄	blue* blue blue	0 0 < 1 10 10	BB
PCl ₃ AsCl ₃	D-line	2-3 0	<u>A</u>
SCI ₂	bluish (continuum extending from yellow to violet)	10	В
BCl ₃ BBr ₃ SiCl ₄ SiBr ₄	grey blue yellow	I-2 3-5 o 5-7	B B B
S ₂ Cl ₂ SCl ₃ PCl ₃ POCl ₃	blue bluish D-line bluish-grey	2-4 10 2-3 7-9	B B A B
COCl ₂ CrO ₂ Cl ₂	D-line bluish-greenish- grey	9-10 10-15	A B
$\begin{array}{c} S_2Cl_2\\ S_2Cl_2 + O_2\\ SCl_2\\ SCl_2 + O_2\\ S_2C\\ S_2C\\ S_2C + O_2 \end{array}$	blue D-line bluish D-line D-line	2-4 > 10 10 > 10 0 > 10 0	B C B C C
$\begin{array}{l} \operatorname{POCl}_{3} \\ \operatorname{POCl}_{3} + \operatorname{O}_{2} \\ \operatorname{CrO}_{2}\operatorname{Cl}_{2} \end{array}$	bluish-grey bluish-grey bluish-greenish-	7-9 7-9 10-15	B B B
$CrO_2Cl_2 + O_2$	bluish-greenish- grey	10-15	В
	* Existence d	loubtful.	

TABLE III.

The luminescences of the reactions of $COCl_2$ and PCl_3 with Na-vapour consist of the D-line; these cases, therefore, probably belong to type A. For $COCl_2$ the reaction might be

(a)	$Na + COCl_2 = NaCl + COCl_2$
(b)	$Na + COCl = NaCl^* + CO,$
(c)	$NaCl^* + Na = NaCl + Na + h\nu$.

The heat of formation of $COCl_2$ from CO and 2Cl-atoms being 82 kCal., and the formation heat of two NaCl (vapour) from the atoms being 190 kCal., either reaction (a) or (b), and possibly even both, might possess a reaction heat of more than 48.5 kCal., which are necessary for the excitation of Na vapour. It seems probable, however, that such a reaction heat is present only in reaction (b). No detailed suggestion can be given for the mechanism of the PCl₃ luminescence.

The luminescence of GeCl_4 is in every respect similar to that of SnCl_4 , and might be accordingly accounted for by a mechanism of type B. Of the other chlorine compounds, only SCl_2 has a considerable intensity of chemiluminescence. Its spectral character appears to be a continuous band, extending from yellow to violet; very similar to the spectrum of the SnCl_4 and GeCl_4 luminescences. On this evidence it might be classified with these in group B. The luminescences of S_2Cl_2 and BCl_3 appear to be of similar character, but the light was too faint to permit a clear determination of the spectral character.

It is interesting to note that the reaction of $SiBr_4$ is luminescent, although that of $SiCl_4$ is not. There is a similar relation between BBr_3 and BCl_3 ; the luminescence of the bromine compound is considerably more intense than that of the chlorine compound. The rather incomplete spectral evidence indicates that the luminescence of $SiBr_4$ and BBr_3 belong to type B.

A very intense luminescence is obtained with CrO_2Cl_2 , and a somewhat less bright one with POCl₃. Both luminescences are not of the colour of the D-line, and in consequence cannot belong to type A, but are probably of the type B.

There is a marked connection between the occurrence of the luminescences which we have classed under the type B, and the velocity of the reaction from which they arise. Of nine substances yielding a luminescence of this type, eight react instantaneously with sodium vapour. BCl_3 , which forms an exception to this rule, gives only a very faint luminescence.

Not only do all luminescences emitting other light than that of the D-line (with one exception) come from instantaneous reactions, but also conversely, all the instantaneous reactions of polyhalides hitherto observed are accompanied by such luminescences.

A further series of luminescences appeared when oxygen was added to the reaction mixtures of CS_2 , S_2Cl_2 and SCl_2 (Table III.). Sodium vapour and oxygen react with one another according to Haber and Sachsse,¹² through the primary formation of NaO₂, which is subsequently stabilized by collisions with the carrier gas; this reaction is accompanied by no visible luminescence. The reaction between sodium vapour and CS_2 is, as was pointed out above, probably of a similar type to that of Na + O₂, and it likewise shows no trace of luminescence; it is only the mixture of O₂, CS_2 and Na which emits light. It is a bright radiation of the colour of the D-line.

The two luminescent reactions of sodium vapour with S_2Cl_2 and SCl_2 are also profoundly modified by the addition of oxygen; a strong emission of the D-line arises in the presence of which the original luminescence can no more be observed; it could not be established whether it had actually vanished, or had only become invisible when outshone by light which arises on the addition of oxygen. Oxygen had no effect on the luminescences of POCl₃ and CrO₂Cl₂.

The luminescences caused by the addition of oxygen resemble the luminescences classed above, under type C, which also require the presence of three reacting substances. We can offer no suggestion for this mechanism, and can note only that sulphur is present in each of the observed cases.

18 Z. physik. Chem., Bodenstein Festband. 1931, 831.

Size of the Luminescent Zone.

The luminescent zone is of the same shape as the area filled with sodium vapour, by which the reaction zone (or "flame") is usually characterised (see Fig. 1). In the cases listed in Table IV. we have

TABLE IV.

Halogen Compound.	Diameter D of the Resonance Flame.	Diameter D' of the Luminescence Flame.	D/D'.
SnCl ₄	1.235	1.03	1.30
,,	1.365	1.03	1.34
	2.41	1.76	1.37
,,	2.95	1.765	1.67
,,	3.42	2.145	1.01
,,	4.14	2.695	1.24
GeCl ₄	1.72	1.24	1.13
PCl _a	2.99	~1.5	~ 2.0
,,	3.66	~ 2.0	~ 1.8
	3.00	~ 2.0	~ 2.0

measured the diameters both of the luminescent zone and of the sodium "flame"; the former appears to be always smaller than the latter. This proves that the light is stronger in the central parts of the "flame"; a fact easily to be explained by relating the intensity of the luminescence to reacting quantities per time and volume unit, which are higher in the interior parts of the flame than at its periphery.

Summary.

I. The reaction velocities of a series of polyhalides $(BCl_3, BBr_3, CCl_4, SiCl_4, SiBr_4, GeCl_4, SnCl_4, TiCl_4, PCl_3, AsCl_3, SCl_2, S_2Cl_2, COCl_2, POCl_5, CrO_2Cl_2) reacting with sodium vapour have been determined by use of the "diffusion method."$

2. Owing to the extreme rapidity of most of the reactions the rates of a few only could be quantitatively determined, while the order of magnitude and the sequence of reactivity were established for the rest. The polyhalides of the elements belonging to the middle groups of the periodic table show the highest inertia in reacting with Na-vapour.

3. In a homologous series the chemical inertia increases with the restoring force acting in the halogen linkage.

4. Na-vapour reacts with CS_2 -vapour; probably by a three-body collision.

5. Thirteen different new luminescences were observed arising from the reactions of Na-vapour with BCl₃, BBr₃, SiBr₄, GeCl₄, PCl₃, SCl₂, S₂Cl₃, COCl₂, POCl₃, CrO₂Cl₂ and from a mixture of Na-vapour and O₂ reacting with CS₃, SCl₂ and S₂Cl₂. A classification of these chemiluminescences according to principles previously established has been attempted.

The above experiments were carried out in the Kaiser Wilhelm Institut für Physikalische Chemie from January to August, 1933. The authors wish to recall in deep gratitude the memory of F. Haber who, during this period, was Director of the Institute.

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