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The Action of "Active" Nitrogen on Iodine
Vapour.

By L. H. Easson, B.Sc., and R. W. Armour, B.Sc.

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I.—The Action of "Active" Nitrogen on Iodine Vapour. By
L. H. Easson, B.Sc., and R. W. Armour, B.Sc. *Communicated*
by Dr E. B. LUDLAM, M.A.

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THE rapid progress which has been made in the last few years in the knowledge of the rotational, vibrational, and electronic energy of molecules has extended the range of chemical investigation, particularly in the region of chemical kinetics. This knowledge is derived chiefly from the study and interpretation of band spectra, and one of the most obvious cases to examine is that of "active" nitrogen which emits a characteristic spectrum and is capable of energetic chemical reaction with a wide range of substances. For most of the early work, including spectroscopic observations, we are indebted to the excellent and thorough investigations of Strutt.

The fact that the yellow glow in nitrogen, produced by a powerful condensed electrical discharge, disappears so slowly that its rate of decay can be measured accurately, suggested that this rate of decay might be made the subject of careful investigation in the presence of foreign gases, and this was the starting-point of the present work. While it was in progress, however, a paper was published in the *Journal of the Chemical Society* by Rideal and Willey (*Journal Chem. Soc.*, July 1926) which pointed to the conclusion that the energy of active nitrogen was much smaller than seemed compatible with the spectroscopic observations. Our experiments with iodine having shown that the reaction of this vapour with active nitrogen was, in the ordinary sense, instantaneous, we turned

our attention to spectroscopic evidence as to the amount of energy communicated to the iodine molecule by the nitrogen. We pointed out, in a letter to *Nature* (Oct. 23, 1926), that Strutt had observed the excitation of the line $206 \mu\mu$ in the spectrum of the blue iodine glow which is produced by the interaction, and for the production of which an amount of energy about four times as great is needed as that postulated by Rideal and Willey.

In a letter in *Nature* (June 25, 1927) Willey outlines new results which he has obtained which go some way to clear up the discrepancy between spectroscopic data and his earlier results, but adequate discussion of this work must be delayed until the details are published. In these latest experiments the glowing active nitrogen is produced in one discharge tube, then passed into another through which a feeble discharge is passing, thereby destroying the glow, but on passing the nitrogen after this treatment into nitric oxide, nitrogen peroxide is produced; even with the feeble discharge alone, which produces no visible glow, abundant formation of nitrogen peroxide is obtained. The conclusion is that the glow is due to the recombination of the atoms, with a heat of formation of the molecule of about 250,000 calories per gram-molecule, and that, nevertheless, the chief constituent is the chemically active form, with an energy content of only about 45,000 calories per gram.-molecule; its nature is admittedly obscure.

In our opinion this recognition of different states of excitation in the gas which leaves the discharge chamber is timely; the use of the word "active" as though it signified one and only one state of activation is no longer appropriate. It may still remain convenient to speak of the glow produced by the condensed discharge as active nitrogen, but it will be understood that the term is being used loosely, in a historical sense, subject to qualification. "Atomic" nitrogen may be an adequate term for the nitrogen atoms, for the line spectrum of nitrogen is no necessary accompaniment of the production of the glow, which is produced by the combination of neutral atoms, but the complex spectrum of the glow is evidence of the many different states of activation which are responsible for the emission of the bands, quite apart from the non-luminous state which Willey concludes to be the major portion.

The spectrum of the yellow glow has been thoroughly studied recently by Birge (*Nature*, 1926, **117**, 81, 300), and Sponer, and also by R. C. Johnston (*Nature*, Jan. 1, 1927). It consists of three groups of bands, (α) a selection of the "first positive" bands of the nitrogen molecule; (β) and (γ) bands due to nitric oxide. With a few per cent. of oxygen the (α)

band is suppressed, but the (β) and (γ) bands persist strongly; being in the ultra-violet they are invisible. With excess of oxygen a green glow is produced but is short-lived.

The spectroscopic evidence in favour of the glow being due to the recombination of atoms is twofold: (*a*) the spectrum of the glow itself, and (*b*) the spectra of other substances which it can excite. The peculiar limitation of the first positive band receives a satisfactory explanation if eleven quanta of vibrational energy (2.1 volts) and 9.3 volts of electronic energy are assumed, the two together giving 11.4 volts, equivalent to 263,000 calories, this being the energy of recombination of neutral atoms.

Evidence of the second type was first emphasized by Saha and Sur; we have pushed it as far as possible with quartz apparatus to the extreme ultra-violet in the case of iodine; Constantinides (*Nature*, Jan. 29, 1927) finds that iodine is actually ionised, which carries the range much further into the Schumann region, indicating an energy beyond 9 volts.

In order to investigate the spectrum of iodine excited by active nitrogen, several different types of apparatus were used. In all cases the nitrogen was rendered active in the discharge bulb A shown in fig. 1 (*a*).

In the first experiment the glass tube (fig. 1 (*b*)) was attached to this bulb; the union was accomplished by tapering slightly the end of this glass tube and pushing the taper into the component of the ground-glass joint fixed to the discharge bulb; the union was then surrounded by a rubber tube, well waxed. A quartz plate was fixed by means of wax on to the other end of this glass tube, and near this end was sealed on a side-tube connected to the pump. A small amount of iodine was introduced into the glass tube through a side-tube (not shown in figure) which was closed by means of a rubber stopper.

A slow stream of purified nitrogen was then passed through the apparatus at such rate that a good bright yellow glow extended right to the iodine, above which a brilliant blue glow was visible. The slit of a small Hilger quartz spectrograph was placed opposite the quartz plate and an exposure of nine hours was given, using an Imperial "Eclipse" plate (H. & D., 650).

On this plate was seen a large amount of fogging in the violet and near ultra-violet, and the iodine line at $206\ \mu\mu$ was very strong. Also, there was very faintly seen a line at about $185\ \mu\mu$.

It was then decided to repeat this experiment using an apparatus which would allow the placing of the slit of the spectrograph very

close to the iodine glow. Also a fluorite window was substituted for a quartz plate, in order to obtain somewhat greater transparency in the region of $180 \mu\mu$. Using this apparatus an exposure of twenty hours was given, employing the same type of plate as previously and treating it with paraffin in order to sensitize it to ultra-violet light of short wave-length.

This plate showed no trace of a line at $185 \mu\mu$, and also the iodine line at $206 \mu\mu$ was very much fainter than on the previous plate.

In both experiments there was a length of glass tubing of 25–30 cms. between the discharge bulb and the iodine, in order to hinder the passage of charged particles from the former to the latter. No doubt such particles could be more completely eliminated by passing the stream of gas between two metal plates with a potential difference applied to them. This method was tried and the line 206 was obtained as before. It must be remembered, however, that the decay of active nitrogen emits ultra-violet light, and therefore there would always exist the possibility of electrons being emitted photo-electrically from the metal plates.

In order to ascertain if the line at $185 \mu\mu$ photographed in the first experiment was really a component of the iodine spectrum, the latter spectrum was photographed directly, using a fused silica tube containing iodine vapour, and provided with external electrodes between which the non-condensed discharge from an induction coil was passed. The photograph thus obtained showed the lines at $206 \mu\mu$ and $185 \mu\mu$, both of which coincided exactly with the lines obtained on the previous plate. Further, the relative intensity of the two lines was very similar on the two plates.

As far as we know, the shortest line previously excited by means of active nitrogen was the iodine line at $206 \mu\mu$ (Hon. R. J. Strutt, *Proc. Roy. Soc.*, 1912, **86** (A), 105). This line gives an energy content for active nitrogen corresponding to 6.0 volts, while the line at $185 \mu\mu$ observed by us corresponds to a voltage of 6.7 volts. We believe, then, that we have extended the spectroscopic evidence for the energy content of active nitrogen from 6.0 to 6.7 volts. Further extension will not be possible by means of the ordinary quartz instruments of the laboratory, as quartz absorbs a large proportion of light of shorter wave-length than $180 \mu\mu$.

From some experiments which he made on the effect of compression on active nitrogen, Strutt early arrived at the conclusion that the process of decay of active nitrogen cannot be of a monomolecular type, and

tentatively suggested that it might be bimolecular. He pointed out, however, that actual determinations of the rate of decay of the active gas were necessary definitely to settle the point. In 1921, Angerer (*Physikal. Zeitsch.*, 22, 97-102) published the results of such determinations carried out by him. By measuring the intensity of the radiation from nitrogen enclosed in a sealed globe and activated by the electrodeless discharge, and by assuming that this intensity was proportional to the amount of active nitrogen present, he obtained results which led him to conclude that the decay of active nitrogen is essentially bimolecular.

The extension of these experiments to cases in which the active nitrogen is not allowed to suffer simple decay, but is made to act on some other substance, is of interest in various ways. For example, it would be of considerable assistance in deciding whether any chemical reaction takes place, with the formation of more or less stable compounds; and in investigating the nature of any such reaction. Certain experimental difficulties, however, arise immediately. These may be stated as follows:—

(1) The active nitrogen is itself decaying and so emitting radiation during the production of radiation by the second substance. (The method is of course only applicable to those cases in which luminosity is produced by the action of the nitrogen on the substance.)

(2) As the nitrogen must be activated before being mixed with the second substance, and the operation cannot therefore be carried out in a simple closed vessel, and as it is very difficult to obtain constancy in all the conditions, it is not possible to introduce a correction for (1) by means of a blank experiment.

(3) If the "reaction" be made more rapid (by increasing the concentration of the second substance), then rate of mixing may become the determining factor in rate of decay.

In spite of these difficulties, however, it was thought that there might be some possibility of obtaining, at least, approximate results for the velocity of such a "reaction," and it was with a view to the settlement of this question that the preliminary experiments about to be described were performed.

The Apparatus Used.—The main portion of the apparatus is shown in fig. 1 (a). The bulb A of about 1500 c.c. capacity constitutes the discharge vessel, having sealed into it two aluminium electrodes (not shown). The exciting discharge is obtained from a large induction coil, a jar and spark-gap being included in the circuit. The bulb A communicated by means

of a wide tube and a tap of 10 mm. bore with a second bulb B of about two-thirds of its capacity. This is the "reaction" chamber, the pressure of iodine in it being controlled by varying the temperature of the tube C, which contains a little solid iodine. These bulbs could be evacuated separately by means of a "Hyvac" two-stage rotary oil-pump, driven electrically. Pressures could be read by a manometer and a McLeod gauge, not shown in the figure. In order to prevent as far as possible radiation from the discharge bulb reaching the window W, the wide tube was bent through about 45° at the dotted line, and the whole of this bulb was encased in a light-tight box.

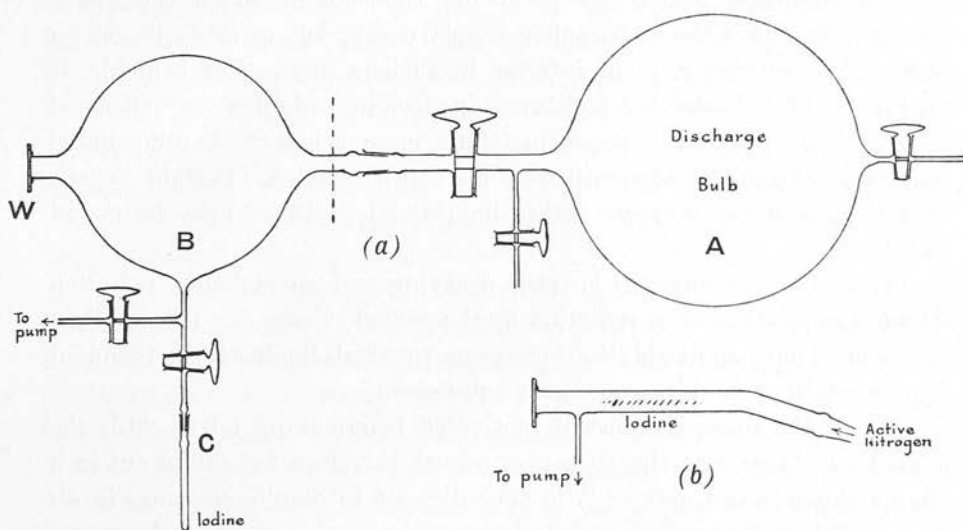


FIG. 1.

The nitrogen used for the experiments was the ordinary commercial gas, purified by passing twice through alkaline pyrogallol, twice through concentrated sulphuric acid, over phosphorus pentoxide, and finally through the liquid alloy of sodium and potassium.

The First Experiment.—The object of this experiment was to determine what pressure of iodine vapour was required in order to make the velocity of the "reaction" with iodine so great that simple decay could be neglected altogether.

It was necessary to devise a method of arriving at some idea of the relative amounts of energy being radiated as ordinary nitrogen afterglow and appearing as radiation from the iodine. At first it was thought that there might be sufficient differences between the photographic properties of these two radiations to enable the desired results to be obtained by

simply placing a photographic plate at a quartz window at W (this window was waxed on, so that it could be made of any desired material), and comparing the depths of the photographic images produced by the total afterglow at various concentrations of iodine vapour. It was found, however, that the images were all of the same density, no matter what the nature of the afterglow. A glass window was now substituted for the quartz one, but with no better results. Various forms of monochromator were also tried, but in no case was there sufficient intensity of radiation to affect the plate at all. The method finally adopted was that of using a light-filter. This consisted of a small glass cell, about 5 mm. in thickness, and filled with a solution of methyl orange in water. The concentration of this was such as to cut off practically all the radiation except that between about 300–370 $\mu\mu$, in which region the strongest bands of the iodine glow lie. The procedure adopted was as follows:—

The bulb B was evacuated to a pressure of about .05 mm., having been previously thoroughly washed out with nitrogen, the tap to the tube C remaining closed. The bulb A was evacuated also to a pressure of 5 mm., and the discharge started. The tap communicating with the bulb B was opened, and the discharge immediately stopped. The photographic plate, which was contained in a holder which exposed only a small area at a time, was placed in contact with the window during this operation.

The bulb B was again evacuated to .05 mm., but this time the tube C was cooled in liquid air and allowed to communicate with the bulb. After about thirty minutes another exposure was made as just described, the photographic plate having been moved to a different position. This was repeated at a number of different temperatures, gradually rising to 16° C.

On developing the plate definite differences in the density of the image was observed as the iodine pressure rose. In the entire absence of iodine the image was only very faint, increasing in intensity until the iodine tube had attained a temperature of somewhere about -15° , above which increase of iodine pressure had very little effect. Now from the results of Haber and Kerschbaum (*Zeitsch. für Electrochemie*, 1914, 20, 302), the vapour pressure of iodine at this temperature is about .005 mm. Also the proportion of active nitrogen in the bulbs is of the order of $2\frac{1}{2}$ per cent. (Strutt, *Proc. Roy. Soc.*, 85, 223; 86, 58). Taking the final pressure in the apparatus as 3 mm., it will be seen that the pressure of iodine required to produce practically nothing but iodine glow is of the order of $\frac{1}{15}$ part of the active nitrogen present. It would appear from this, taken in con-

junction with the fact that the glow is practically instantaneous in these circumstances, that any chemical action is extremely unlikely, the iodine merely receiving energy and radiating it over and over again. This view receives additional support from the facts that at about -50° (the lowest temperature investigated by Haber and Kerschbaum) there is a very decided photographic effect from the iodine, the pressure of the vapour at this temperature being less than $\cdot 00006$ mm., or $\frac{1}{1250}$ of the partial pressure of active nitrogen; and that at even a lower pressure of iodine a considerable and comparatively short-lived blue glow was observed visually.

Second Experiment.—During the course of the experiments just described it had been noticed that, as had been expected, the duration of the luminosity when the iodine pressure was such as to produce the greatest photographic effect was so small as to cause the glow to appear instantaneous to the eye. We therefore endeavoured to obtain the order of this velocity by the use of a kinematographic camera. This was a small pocket model of extremely short focal length. The lens was placed close to the window of the same apparatus as was used in the first experiment. The iodine tube was maintained at a temperature of 0° C. The procedure was exactly as before, except that the discharge was not stopped immediately after opening the tap. The exposure was started just before opening the tap, and stopped after the blue flash had taken place. This was repeated several times, at increasing camera speeds.

When the film was developed it was found that previous to opening the tap no mark had been made on it, but that when the tap had been opened a slight image always appeared, due in all probability to reflected light passing through the tap. In some cases, however, a single strong exposure was obtained. In no case was there more than one of these. It would, therefore, appear that the duration of the blue glow is less than the interval between successive exposures at the most rapid camera speeds used. In fact, it must be considerably less, as in a large number of cases no exposure of this kind was produced at all, so that in these cases the flash must have begun and ended between two exposures. (It was estimated that the greatest speed attained with the camera was more than one hundred exposures per second.)

These results led us to the conclusion that if the velocity of the "reaction" with iodine is made high enough to eliminate the effect of the decay of the active nitrogen, then this velocity is too great to allow of its measurement by ordinary means. That the rate of "reaction" was largely influenced by rate of mixing of the two gases was in fact directly

observable, a distinct streaming of the blue luminescence being noticed where the active nitrogen issuing from the tap came into contact with the iodine vapour.

Conclusions.—Spectroscopic observation shows that glowing "active" nitrogen can excite the line $185\mu\mu$ in the spectrum of the iodine atom; there is, therefore, some form of nitrogen present capable of imparting an energy sufficient to dissociate the iodine and raise the atom to the level of electronic energy necessary for it to emit this line, a total of $35,000 + 154,000 = 189,000$ calories, equivalent to $1.7 + 6.7 = 8.4$ volts. This supports the view that the glow is produced by the combination of atoms of nitrogen, which accounts for the high energy level. When the pressure of iodine vapour is of the same order as that of the "active" nitrogen, the visible reaction is an instantaneous flash, which even with imperfect mixing, did not last one hundredth of a second.

Our thanks are due to Professor Sir James Walker and Dr E. B. Ludlam for their interest and advice, and to Messrs Brunner, Mond & Co. for a grant to defray some of the cost of apparatus.

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(Issued separately February 9, 1928.)

THE PHOTOCHEMICAL EQUILIBRIUM OF HYDROGEN
BROMIDE EXPOSED TO LIGHT IN THE
EXTREME ULTRAVIOLET.

by

ROBERT WILLIAM ARMOUR, B.Sc.

Thesis for the Degree of Ph.D. 1929.



THE PHOTOCHEMICAL EQUILIBRIUM OF HYDROGEN BROMIDE
EXPOSED TO LIGHT IN THE EXTREME ULTRAVIOLET.

INTRODUCTORY.

The fact that light is necessary for the progress of some chemical reactions has been known ever since it was recognized that plants could only assimilate their nourishment in sunlight. In more recent times, the processes of photography have furnished the most striking examples of the photochemical reaction.

In the development of photochemistry as a science, two hypotheses must be considered as of supreme importance, as they have led to so much research. The first of these is the Quantum Theory, put forward by Planck in 1900. Though this theory has no direct connection with photochemistry, its importance lies in the fact that it led directly to the second of the two hypotheses, namely the Law of Photochemical Equivalence, put forward by Einstein (Ann. Physik. IV, 37, 832; 1912; also *ibid.* IV, 17. 132; 1905), which supplies an explanation of the mechanism of the photochemical reaction from the point of view of the Quantum Theory. The testing of the validity of this hypothesis has led to some of the most brilliant work in/

in this branch of physical chemistry, especially by Warburg (Sitz. König. Preuss. Akad. Wissen., 1912-1918).

It was early recognised that to be effective in producing a photochemical change in a substance, the light employed must be of a wave-length which is absorbed by that substance. Hence the study of photochemistry has always been intimately linked with the investigation of the absorption spectra of substances. In the case of organic compounds, this particular branch of the subject has made great strides within recent years, since it has been discovered that there is a fairly close relationship between the structure of a substance and its absorption spectrum.

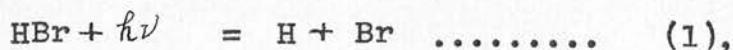
Photochemical reactions have been studied for substances in solution, in the solid state, and in the gaseous state. As in other branches of chemistry, the gaseous state is by far the simplest from the point of view of theoretical treatment, and most photochemical work of a quantitative kind has been performed in the case of substances in this state.

THE PHOTOCHEMISTRY OF THE HYDROGEN HALIDES.

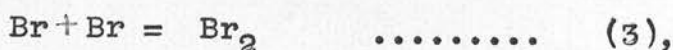
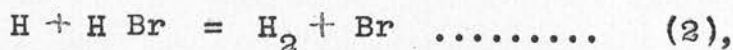
In the whole region of photochemistry, probably no series of compounds has been more fully investigated than that of the compounds of the halogens with hydrogen. The modern study of the photochemistry of/
of/

of these compounds may be said to date from 1912, when Warburg and Bodenstein applied the quantum conceptions of Planck to this branch of chemistry, and in the same year Einstein introduced his law of photochemical equivalence.

Warburg (Sitz.König.Preuss.Akad.Wissen., 1912-1918), in his classical series of researches on the validity of Einstein's law, investigated the photolysis of hydrogen bromide and hydrogen iodide from the point of view of this law. He found that with both these compounds the ultimate result of this photolysis was the decomposition of two molecules of hydrogen halide per quantum of radiation absorbed; this is explained by assuming that the primary reaction obeys Einstein's law exactly, and consists in the decomposition of one molecule of hydrogen halide per quantum:-

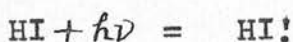


and it can then be shown that the following secondary reactions will take place independent of the radiation, and, in particular, that they are the only reactions thermodynamically possible:-



so that the final effect of the radiation is the decomposition of two molecules of hydrogen halide per quantum/

quantum of light absorbed. In the case of hydrogen iodide, Warburg's results have been confirmed by Bodenstein and Lieneweg (*Z. physikal. Chem.*, 119, 123; 1926). As an alternative explanation of the mechanism of this photolysis, Stern and Volmer (*Z. Wiss. Phot.*, 19, 275; 1920) suggested that the primary reaction consisted in the production of an 'activated' hydrogen halide molecule by its absorption of a quantum of radiation, and that this molecule by collision with a normal molecule brings about the decomposition of both:-

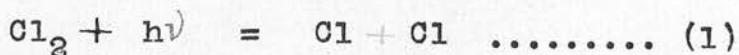


so that again two molecules are decomposed for each quantum absorbed. For hydrogen iodide, however, it has been shown by B. Lewis (*Nature*, 119, 493; 1927), that at very low pressures the quantum efficiency of the reaction is the same, viz., two, as at ordinary pressures, and, since the life of an activated molecule must be very short (about 10^{-7} sec.), the occurrence of collisions cannot be essential for the decomposition of the hydrogen iodide molecule, and hence it must be concluded that Warburg's explanation of the mechanism of the reaction is preferable.

Warburg's work, and especially the above quoted example of the photolysis of hydrogen bromide and hydrogen iodide, has led to the conclusion, now generally accepted, that Einstein's law is universally valid/

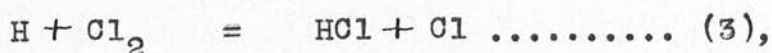
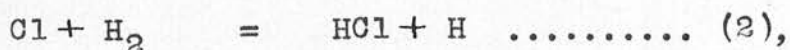
valid for the primary reaction produced by the light, though in probably the large majority of cases, at least with the reactants present at ordinary pressures or concentrations, the primary reaction is obscured by subsequent secondary reactions.

In connection with the photosyntheses of hydrogen chloride and hydrogen bromide from their constituent elements, it is well known that the union of hydrogen and chlorine takes place explosively in bright light, and that even with feeble illumination a considerable amount of hydrogen chloride is formed, so that a mixture of hydrogen and chlorine has been made use of as an actinometer by measuring the amount of hydrogen chloride formed. Calculations on this reaction, based on the experiments of Bodenstein and Dux (*Z. physikal. Chem.*, 85, 297; 1913), by Bodenstein (*ibid.*, p. 333), and Gohring (*Z. Elektrochem.*, 27, 511; 1921), led to the conclusion that at ordinary pressures about 500,000 molecules of hydrogen chloride are produced per quantum of radiation absorbed. Nernst (*Z. Elektrochem.*, 24, 335; 1918) explains this by stating that the primary photochemical reaction obeys Einstein's law, and consists in the decomposition of one chlorine molecule by one quantum of light into chlorine atoms:-



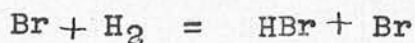
He then states that this is followed by two secondary reactions.

Cl/



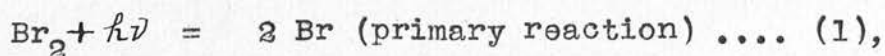
and by successive repetitions of (2) and (3), a chain of reactions is set up, so that the number of molecules of hydrogen chloride ultimately formed is very large; indeed it would appear that the above series of reactions could only be stopped by the union of the hydrogen or chlorine atoms, or of the chlorine and hydrogen atoms. It can be shown by means of the Nernst heat theorem that both reactions (2) and (3) are thermodynamically possible, and recent optical measurements on the energy of dissociation of chlorine and hydrogen show that reaction (2) is feebly exothermic while (3) is strongly so.

The photosynthesis of hydrogen bromide differs from that of hydrogen chloride in that it does not take place explosively, and corresponding to this it is found that even strong illumination results in the formation of but little hydrogen bromide. Evidently in this case the chain series of reactions is not possible, and this is proved by Nernst (*loc.cit.*) by means of his heat theorem, which shows that the reaction:—



is thermodynamically impossible. This particular case/

case of photosynthesis has been most carefully studied by Bodenstein and Lutkemeyer (Z. physikal. Chem., 114, 208; 1924), who show that the mechanism of the reaction is somewhat complicated, as no less than four secondary reactions take place following the primary photochemical change, which obeys Einstein's law:-



This mechanism leads to the following result for the rate of formation of hydrogen bromide, $\frac{d(\text{HBr})}{dt}$:-

$$\frac{d(\text{HBr})}{dt} = k_1 \frac{\sqrt{N} [\text{H}_2]}{1 + k_2 \frac{[\text{HBr}]}{[\text{Br}_2]}} \dots (6),$$

where k_1 and k_2 are constants, and N is the number of quanta of radiation absorbed by the bromine in unit time. This expression is completely confirmed by experiment, which shows that the rate of formation of hydrogen bromide is directly proportional to the pressure of hydrogen, and that the reaction is accelerated by increase in the pressure of bromine and retarded by increase in that of hydrogen bromide. The most important experimental confirmation, however, lies in the fact that the amount of hydrogen bromide formed in unit time is proportional to the square root of the number of quanta absorbed. That is, the velocity of formation of hydrogen bromide from its /

its constituent elements is directly proportional to the square root of the intensity of illumination; as may be seen from the primary reaction (1), this means that the rate is proportional to the concentration of bromine atoms in the system. This reaction, therefore, furnishes an apparent exception to the Grotthus-Draper law, and gives a good example of the fact that it is extremely difficult to check the accuracy of any hypothesis about the mechanism of a purely photochemical reaction, as the changes brought about by this latter may be almost completely obscured by subsequent secondary reactions.

In connection with this reaction, Bodenstein and Lind (Z. physikal. Chem., 57, 168; 1906) showed that the rate of formation of hydrogen bromide in the dark could be represented by a similar expression, in which the square root of the concentration of the bromine was substituted for the square root of the intensity of the illumination, viz:-

$$\frac{d(\text{HBr})}{dt} = k_1 \frac{[\text{H}_2] [\text{Br}_2]^{1/2}}{1 + k_2 \frac{[\text{HBr}]}{[\text{Br}_2]}}$$

so that the velocity of the reaction is again proportional to the concentration of bromine atoms. This proves that the kinetics of the photochemical and thermal formation of hydrogen bromide are precisely the same, except that in the first case the bromine atoms are produced by the action of light, while in the/

the second the thermal energy of the bromine molecules produces bromine atoms by dissociation.

It should be noted that though the kinetics of the union of bromine with hydrogen are somewhat complicated, the photochemical union of bromine with some organic substances follows Einstein's law in a very simple manner. Thus it has been shown by Nernst and Pusch (Z.Elektrochem., 24, 335; 1914) and by Noddack (Z.Elektrochem., 27, 359; 1921), that in the reaction between hexahydrobenzene and bromine, the absorption of one quantum of energy leads to the disappearance of one molecule of bromine.

Einstein's law postulates that in a photochemical reaction, a certain minimum, or threshold frequency is necessary for the light involved, in order that the quanta may contain sufficient energy to produce the reaction. Now in the photosynthesis of the halogen hydrides the primary reaction consists in the splitting of the halogen molecule into atoms, and so it becomes interesting to investigate what frequency of radiation is necessary for this purpose. In this connection it has been shown by Franck (Trans. Far. Soc., 21, 536; 1925) that the halogens exhibit in their absorption spectra a series of bands converging to a limit, or 'Konvergenzstelle', the wavelength of which corresponds to the amount of energy necessary to dissociate/

dissociate the halogen molecule into a normal and an excited atom. In order, then, that the light should be effective in producing photosynthesis of the halogen hydrides, it is necessary that its wave-length should be not longer than this limiting value, and as it is also necessary that a certain amount of surplus energy be supplied, the light must be of somewhat shorter wave-lengths. It should be remembered that the actual threshold value of the wave-length will be to some extent influenced by the temperature, and up till now but little exact quantitative work has been done on the subject, so that Franck's indirect treatment of the problem supplies figures which, though probably only approximately indicating the position of the threshold wave-length, are the only ones available at the present time.

In the case of chlorine and bromine, the 'Konvergenzstellen' are situated at wave-lengths 478.8 $\mu\mu$ and 510 $\mu\mu$ respectively, and as the absorption bands of both these substances lie at considerably shorter wave-lengths (350 $\mu\mu$ and 420 $\mu\mu$ respectively), it will be seen that light absorbed by these halogens will be capable of producing the photosynthesis of their hydrides. With iodine, however, both the 'Konvergenzstelle' and the absorption band in the visible lie at 500 $\mu\mu$, and consequently light in the visible/

visible spectrum absorbed by this halogen has not sufficient energy to produce the photosynthesis of hydrogen iodide.

This leads to the consideration of the effect of light of different wave-lengths on the photosynthesis and photolysis of the halogen hydrides. The problem has been investigated by Coehn and Stuckardt (Z.physikal. Chem., 91, 122, 1916), who performed work on the equilibrium between these compounds and their constituent elements under the influence of light of different wave-lengths, and also discussed the relationship between the position of equilibrium and the absorption spectra of the components of the system. Since the research to be described is an extension of that of Coehn and Stuckardt, it is desirable to examine the work of these authors somewhat closely.

It is well known that the spectral properties of the three halogens - chlorine, bromine and iodine - resemble each other closely, and that the corresponding spectral characteristics show a displacement towards the longer wave-lengths on passing from chlorine to iodine. Coehn and Stuckardt (loc.cit.) have demonstrated this fact for the absorption spectra, not only of the halogens themselves, but also of their compounds with hydrogen. In addition, Ludlam and West (Proc.Roy.Soc.Edin., 44 II, No.17) have shown that/

that the emission spectra of the three halogens exhibit this property.

It seems then reasonable to anticipate that the state of the photochemical equilibrium in the reaction:-



(where X represents Cl, Br or I,)

will be related to this property of the absorption spectra of the gases involved. For the purpose of the investigation of the equilibrium under the influence of light of different wave-lengths, monochromatic light ought to be employed, but up to the present it has been found impossible to obtain such light (in the ultraviolet especially) of sufficient intensity. In their researches, therefore, Coehn and Stuckardt employed a mercury vapour arc as source of illumination, and investigated the equilibrium (1) under the full radiation from the lamp, (2) with the spectrum terminated at $254 \mu\mu$ by means of a 'Uviol' glass screen, and (3) with the spectrum cut off beyond $300 \mu\mu$ by 'Jena' glass. It would appear from the results obtained that in many cases effects which can only be attributed to the shortest wave-lengths present in the radiation seem greatly to preponderate over those arising from the longer wave lengths.

Briefly, Coehn and Stuckardt's results were as/

as follows:-

Hydrogen Iodide. With the spectrum extending either to $300\mu\mu$ or to $254\mu\mu$, equilibrium lies at complete decomposition. With the full spectrum, reaching to $220\mu\mu$, 7.5 per cent of hydrogen iodide is present at equilibrium.

Hydrogen Bromide. With the spectrum cut off at $300\mu\mu$, complete formation of hydrogen bromide takes place; with the full spectrum, equilibrium lies at complete decomposition, while in the intermediate case, with the spectrum extending to $254\mu\mu$, 80 per cent of hydrogen bromide is present at equilibrium.

Hydrogen Chloride. Under the influence of the full radiation of the mercury arc, traces (<1 per cent) of decomposition appear. With the other conditions, equilibrium lies at complete formation.

On comparing these results with the absorption spectra of the three halogens and their hydrides, it is seen that in a spectral range where the halogen absorbs, formation of the hydride is produced, while in a range where the halogen hydride is the more active absorbent, decomposition of the latter tends to take place.

Thus if we examine in some detail the system of iodine (and hydrogen) and hydrogen iodide, it is seen that the former absorbs in the green of the spectrum and also in the further ultraviolet, while absorption/

absorption by hydrogen iodide also takes place in this latter region; however the absorption coefficient of the halogen hydride rises much more rapidly with decreasing wave-length than that of the halogen. Thus hydrogen iodide is virtually opaque at $280\mu\mu$, while iodine is not so till beyond $230\mu\mu$. In accordance with this, we find that with the radiation reaching to $300\mu\mu$ or $254\mu\mu$, complete decomposition of the halogen hydride takes place, as under these circumstances the latter is the active absorbent. However, if the spectral range be extended to $220\mu\mu$, where absorption by the iodine in the ultraviolet becomes comparable to that by hydrogen iodide, 7.5 per cent of the latter remains undecomposed at equilibrium. It might be expected that light of wave-length about $500\mu\mu$ would cause the formation of hydrogen iodide, since light of this wave-length is absorbed by iodine only. However, the work of Franck (loc. cit.) has shown that light of this wave-length does not possess sufficient energy to bring about the reaction.

In the case of hydrogen bromide, we find the same characteristics of the photochemical equilibrium occurring in definite spectral ranges, but in each case the wave-length is shorter than in the corresponding spectral range for hydrogen iodide. Thus analogous to the absorption band of iodine at $500\mu\mu$, and the formation of hydrogen iodide which might be expected/

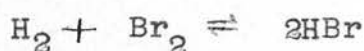
expected (but for the work of Franck) to be brought about by light of this wave-length, there is the absorption band of bromine at $420\mu\mu$, and also it is found that light of wave-length not shorter than $300\mu\mu$ produces complete formation of hydrogen bromide. Absorption by hydrogen bromide does not become considerable till $240\mu\mu$, and hence the complete decomposition of this substance requires light of wave-length $220\mu\mu$, in contrast with $300\mu\mu$ for hydrogen iodide. Extending this comparison further, it is seen, that, corresponding to the ultraviolet absorption band of iodine, absorption by bromine begins at about $220\mu\mu$, and it will presumably increase with decreasing wave-length. Moreover, since light of wave-length $220\mu\mu$ causes a partial formation of hydrogen iodide, one would expect that light of somewhat shorter wave-length might induce partial formation of hydrogen bromide from its elements. To test the validity of this hypothesis, the work described below was undertaken.

The shortest wave-length present in the light used by Coehn and Stuckardt was $220\mu\mu$. It was therefore decided to extend their research, in the case of hydrogen bromide, to the shortest wave-length possible with ordinary quartz apparatus, viz. about $185\mu\mu$. The object of the work was therefore twofold/

twofold:- (a) to examine whether any trace of formation of hydrogen bromide could be detected when a mixture of hydrogen and bromine was subjected to light of wave-length $185\mu\mu$, and, if possible, to determine the amount of halogen hydride present at equilibrium; and (b) to measure quantitatively the coefficient of absorption of bromine in the further ultraviolet as far as this wave-length, that is, in the spectral range $254\mu\mu - 185\mu\mu$.

PART I.EXPERIMENTAL WORK ON THE FORMATION OF HYDROGENBROMIDE FROM HYDROGEN AND BROMINE.

The ideal method of investigating the equilibrium state of the system:-



would be to seal up hydrogen bromide or a mixture of its constituent elements in a suitably transparent vessel, and expose the latter to monochromatic light of wave length 185μ for a period of time sufficient to allow the system to reach its final state of equilibrium. This procedure, however, involves many difficulties. In the first place, only fluorspar is perfectly transparent to light of such wave-length, though crystalline quartz is nearly so; it is not safe, however, to employ a glass vessel provided with a window of one of these substances, as no cement is known which can be relied upon to withstand attack by bromine for a long period, and any action between the cement and bromine would introduce errors into the final state of equilibrium. The only alternative would be to employ a vessel of fused silica; a good specimen of this substance about 1 mm. thick will transmit 80 per cent. of radiation of wave-length 185μ falling upon it. In this case, however, difficult-

ies/

difficulties arise in determining the initial and final states of the system, since the reactants are sealed up in a closed vessel. It was therefore decided, before attempting to measure quantitatively the ultimate state of equilibrium, to perform an experiment designed merely to determine qualitatively whether any trace of formation of hydrogen bromide could be detected when a mixture of hydrogen and bromine was subjected to light to wave-length $185\mu\mu$.

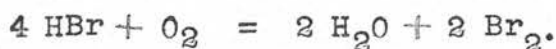
Another modification of the ideal experimental procedure had also necessarily to be adopted. No source of light exists which emits monochromatic light of wave-length $185\mu\mu$, and hence such radiation can only be obtained by means of a monochromator, and this entails the enfeeblement of the radiation to such an extent that no appreciable photochemical change could be expected within reasonable time. It was therefore decided to follow Coehn and Stuckardt's method and to employ radiation consisting of a heterogeneous mixture of different wave-lengths extending as far as $185\mu\mu$. Under these circumstances, it was then necessary to show that any photochemical change produced could only be attributed to the action of the shortest wave-lengths present in the radiation. In the case of the system under investigation, it is known from the work of Coehn and Stuckardt that under the influence of the full radiation from the mercury arc/

arc (extending to $220\mu\mu$), equilibrium lies at complete decomposition of the hydrogen bromide into its constituent elements. Hence, any formation of hydrogen bromide taking place under the influence of light containing radiation of shorter wave-length than this, can only be attributed to the effect of these shorter wave-lengths. Further evidence in this connection is described later.

A search was first made for a suitable source of light, the spectrum of which should extend as far as $185\mu\mu$. The light emitted from a discharge tube, provided with a quartz window and containing hydrogen at a relatively high pressure (0.5 mm), yielded, under suitable conditions, a continuous spectrum extending as far as this wave-length, but it was found impossible with this source to provide a sufficient intensity of illumination. On the other hand, the aluminium spark seemed particularly suitable as a source of radiation, as it gives a strong group of lines near $185\mu\mu$, and further provides the nearest known approximation to monochromatic light of this wave-length, as it has been shown by Pflüger (Ann. Physik., 13, 890; 1904) that more than 35 per cent. of the energy radiated from this source consists of light of this wave-length. Hence it was decided to subject a mixture of hydrogen and bromine to light from this source, and to attempt to detect qualitatively/

qualitatively any formation of hydrogen bromide which might occur.

For this purpose, an apparatus, part of which is shown in fig.1, was constructed. It was necessary that the mixture of hydrogen and bromine should be free from traces of oxygen, as, under the influence of light, this substance decomposes hydrogen bromide thus:-



To this end, the hydrogen used was prepared by electrolysis of 20 per cent sodium hydroxide solution, and was passed through the tungsten filament electric lamp (115 volts, 100 watts) E, which was supplied with sufficient electric current to maintain the filament at a bright red heat. Any traces of oxygen present in the hydrogen were here converted into water, which was removed by means of the calcium chloride tube C and the phosphorus pentoxide bulb P₁. The hydrogen was then passed through bromine in the bubbler B₁, which consisted of a tube about 20 cm. long filled with bromine, and very slightly inclined to the horizontal; the bromine could be introduced as required from the funnel F by means of the stopcock T₂. The resultant mixture of hydrogen and bromine contained the latter gas at a partial pressure of about 110 - 140 mm., this being the vapour pressure of bromine at room temperatures. This mixture of gases was dried in/

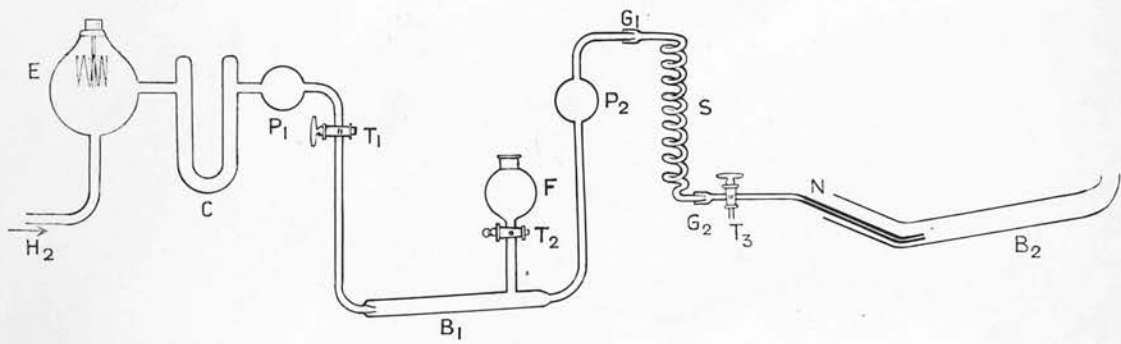


Fig. 1.

in the phosphorus pentoxide bulb P_2 , and then passed through the spiral S, made of thin walled transparent silica tubing, and attached to the remainder of the apparatus (constructed entirely of glass) by means of the ground joints G_1 and G_2 , which were sealed externally with paraffin wax. Finally, the gases were led by means of the narrow-bored tube N into water contained in the bubbler B_2 , consisting simply of a bent, wide glass tube (3 cm. bore), which could be removed when desired. Any hydrogen bromide which might have been formed was hereby dissolved along with the bromine, and the resulting solution was analysed as described later.

By means of the three-way tap T_3 , the apparatus was exhausted previous to the commencement of experiments; by repeated evacuation and filling with hydrogen, all traces of air could be removed. The stopcocks T_1 , T_2 and T_3 , which were exposed to the action of bromine, could not be lubricated with any organic grease; hence syrupy phosphoric acid was employed as a lubricant.

All phosphorus pentoxide used was freed from lower oxides of phosphorus, which are volatile, by sublimation over platinized asbestos in a current of oxygen. The bromine was purified as follows. After washing with water, it was dissolved in a concentrated solution/

solution of pure potassium bromide, and the solution was decanted from any insoluble residue (presumably organic matter). The bromine was recovered from this solution by distillation in steam, and in this way it was freed from chlorine and any organic matter insoluble in potassium bromide solution. The bromine was then distilled over a mixture of calcium bromide and quicklime, to remove water and hydrogen bromide, and finally it was shaken up with, and then distilled over, phosphorus pentoxide (purified by sublimation as described above) in an atmosphere of nitrogen, in order that the resultant pure bromine might contain as little dissolved oxygen as possible. All these manipulations were conducted in apparatus consisting exclusively of glass, and the purified bromine was stored in a 'Jena' glass bottle. It was proved by test to be free from chlorine, iodine, organic matter and sulphuric acid.

The aluminium spark was placed in the centre of the silica spiral S. The spark was fed from a transformer and condenser and consumed about 500 watts, at a pressure of 9,000 volts. The intensity of the spark could be varied within wide limits by altering the capacity of the condenser, and was judged by measuring the amount of light radiated at wave-length $185\mu\mu$ by means of a photoelectric cell, by a method which/

which is described later. The electrodes consisted of aluminium tubes 2 cm. in diameter, cut obliquely at the spark-gap ends. This form of electrode possesses the advantage that it is kept cool by convection currents. The spark-gap between the electrodes was kept at the maximum width (about 7 mm.) at which a steady discharge could be maintained, as it was found that under these circumstances the radiation from the spark contained the greatest proportion of light of short wave-length.

After the apparatus had been in use for some time, a yellowish-white deposit gathered on the walls of the electric lamp, E. This substance was presumably an oxide of tungsten, but it exhibited the curious phenomenon of turning black some time after the lamp had been extinguished and the walls had cooled. This change of colour did not always take place, and the time-interval between the extinguishing of the lamp and the occurrence of the change varied from a few minutes to several days. Invariably, however, on relighting the lamp, the colour turned back to yellowish-white immediately the walls of the lamp were warmed. The only explanation which can be offered is that the substance constituting the deposit exists in two forms, the yellowish-white variety being the stable one at higher temperatures.

In/

In order to prevent the action of visible light in causing the union of hydrogen and bromine, the apparatus was kept in a darkened room, and the aluminium spark and spiral S were enclosed in a light-tight box. Also, when the apparatus was standing for any length of time out of use and with the gas-stream stopped, the tap T_2 was closed, in order to prevent the bromine from diffusing backwards into the lamp E. When operations were again started under these conditions, the three-way tap T_3 was opened to the air and a rapid stream of hydrogen was passed through the apparatus for three hours, in order to remove any traces of hydrogen bromide which might have accumulated, due to the prolonged contact of the bromine with hydrogen. This same precaution was adopted after a fresh supply of bromine had been introduced into the bubbler, B_1 .

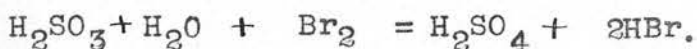
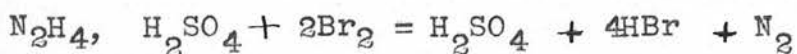
A suitable analytical method was next evolved to determine the amounts of bromine and hydrogen bromide dissolved in B_2 . The estimation of the free bromine presented little difficulty, as it could be determined by addition of potassium iodide and titration of the liberated iodine with standard sodium thiosulphate solution. In freshly made pure bromine water, the amount of free bromine as determined by this method is identical with the total bromine present in the solution (determined as described/

described below), but owing presumably to the hydrolysis of the bromine followed by the formation of various higher oxyacids of bromine, the amount of free bromine quickly becomes less than the total amount of bromine present. The change is very slow in commencing if the temperature be below 12°C , but when once started seems to proceed fairly rapidly. However, by keeping the water in B_2 cold, and by determining the concentration of the free bromine as quickly as possible, it was found easy to obtain perfectly consistent results.

The direct determination of the amount of hydrogen bromine present in the solution was not possible in presence of the bromine, and it was therefore decided to estimate the total amount of bromine present in the solution as free bromine and hydrogen bromine. To this end, the free bromine was reduced to hydrogen bromide, and the total concentration of the latter determined in the usual way by titrating with silver nitrate and ammonium thiocyanate (Volhard's method). The actual experimental procedure for the determinations of the amounts of free and total bromine present in the solution in B_2 was as follows. The solution in B_2 was poured into a bottle and thoroughly shaken; two equal volumes of this solution were then withdrawn by means of a pipette, and in the one the concentration of the free bromine was determined, /

determined, and in the other that of the total bromine. Thus the difference between the concentrations of the free bromine and the total bromine gives the amount of hydrogen bromide originally present in the solution.

The reduction of the bromine to hydrogen bromide was performed by means either of hydrazine sulphate or sulphurous acid:-



In the case of reduction by sulphurous acid, it was subsequently necessary to pass a slow stream of nitrogen through the gently boiling solution, in order to eliminate the excess of sulphur dioxide before the addition of the silver nitrate. Previous to this operation, the solution was diluted so that the concentration of hydrogen bromide was about N/100, so that no appreciable amount of hydrogen bromide could be eliminated along with the sulphurous acid. It was not necessary to destroy the excess of hydrazine sulphate, but it was suspected that this substance had an adverse influence on the sharpness of the end-point of the thiocyanate titration, owing, no doubt, to the slow reduction of the ferric indicator by the hydrazine sulphate.

The standardisation of the sodium thiosulphate and silver nitrate solutions was performed by means of/

of Merck's potassium dichromate and Kahlbaum's potassium bromide respectively, but it was not considered wise to base results on the absolute values of the differences between the concentrations of the free bromine and total bromine, as these values depend not only on the figures adopted for the concentrations of the sodium thiosulphate and silver nitrate solutions, but also, to a certain extent, on the experimental conditions, in that the temperature of the water in B₂ has a small effect on the value obtained for the free bromine. Hence the procedure adopted was to determine the excess total bromine under 'dark' conditions, i.e. with the source of illumination of the silica spiral out of action, and thus perform what may be called a blank, and then to repeat the experiment under the same conditions with the aluminium spark on. The difference between the absolute amounts of hydrogen bromide apparently present in the two cases gives the true amount of this substance formed by the action of the radiation from the source of illumination. 'Blanks' and experiments proper were performed as much as possible alternately throughout the series of determinations. It is interesting to note that on days when the 'blanks' gave high values for the absolute concentration of hydrogen bromide, the/

the experiments proper also tended to yield high values, and when the blanks assumed lower figures, these obtained from the experiments proper were also low.

EXPERIMENTAL RESULTS.

The results are divided into three groups, as the experimental conditions varied slightly in the three cases. In group I the radiation from the aluminium spark was about one tenth the intensity of its values in groups II and III. Sulphurous acid was used exclusively as the reducing agent in the determination of total bromine in groups I and II, and also in group III, except in those cases where the number of the experiment is marked with an asterisk (*), when the reducing agent was hydrazine sulphate.

Group I. /

GROUP I.

(a) 'Blanks'

Normality of sodium thiosulphate solution:- 0.1043 in Nos. 1 & 2
 0.1044 in " 3 - 7
 Normality of silver nitrate solution:- 0.09925 in " 1 - 5
 0.09930 " " 6 & 7
 10.00 cc. ammonium thiocyanate solution are equivalent to"-
 10.56 cc. silver nitrate solution in Nos. 1 - 5.
 10.60 cc. " " " " " 6 & 7.

No.	$\text{Na}_2\text{S}_2\text{O}_3$ Titration c.c.	Normality of free Br_2	AgNO_3 added c.c.	NH_4CNS Titration c.c.	AgNO_3 required c.c.	Normality of total Br_2	Excess total Br_2 per cent. ²
1.	11.06	0.04361	14.33	1.67	12.57	0.04638	+0.55
2.	28.87	0.1205	35.97	3.04	32.76	0.1209	+0.36
3.	15.02	0.06273	17.52	0.48	17.01	0.06275	+0.02
4.	28.84	0.1204	34.77	2.00	32.66	0.1205	+0.05
5.	23.79	0.09938	27.76	0.78	26.98	0.09958	+0.22
6.	26.33	0.1100	29.91	0.04	29.87)	0.1103	+0.30
			29.99	0.11	29.87)		
7.	17.13	0.07154	21.62	2.06	19.44	<u>0.07179</u>	+0.37

Mean value of excess total bromine:- $+0.27 \pm 0.07$ per cent.
 Mean error in each determination of excess total
 bromine:- ± 0.17 per cent.

(b) Experiments with the aluminium spark in operation.

Normality of Sodium Thiosulphate solution:- 0.1043 in No. 1.
 0.1044 " Nos. 2 - 7
 Normality of Silver nitrate solution:- 0.09225 " " 1 - 5
 0.09230 " " 6 & 7
 10 cc. ammonium thiocyanate solution are equivalent
 to:- 10.56 cc. silver nitrate solution in Nos. 1 - 5.

No.	$\text{Na}_2\text{S}_2\text{O}_3$ Titration c.c.	Normality of free Br_2	AgNO_3 added c.c.	NH_4CNS Titration c.c.	AgNO_3 required c.c.	Normality of total Br_2	Excess Total Br_2 per cent.
1.	12.22) 12.22)	0.05098	17.93	3.72	14.00	0.05166	+1.35
2.	16.82	0.07025	22.29	2.83	19.30	0.07122	+1.40
3.	19.46	0.08126	24.12	1.82	22.20	0.08192	+0.85
4.	20.98	0.08763	25.26	1.29	23.90	0.08819	+0.68
5.	18.45	0.07706	21.65	0.55	21.07	0.07774	+0.93
6.	21.46	0.08963	26.09	1.48	24.52	0.09057	+1.05
7.	16.41	0.06853	20.17	1.31	18.78	<u>0.06935</u>	+1.20

Mean value of excess total bromine + 1.07 ± 0.10 per cent.

Mean error in each determination of excess total
 bromine:- ± 0.26 per cent.

GROUP II.

Normality of sodium thiosulphate solution:- 0.09725
 Normality of silver nitrate solution:- 0.08973
 10.00 cc. ammonium thiocyanate solution are equivalent
 to 9.79 cc. silver nitrate solution.

(a) 'Blanks'

No.	$\text{Na}_2\text{S}_2\text{O}_3$ Titration c.c.	Normality of free Br_2	AgNO_3 added c.c.	NH_4CNS Titration c.c.	AgNO_3 required c.c.	Normality of total Br_2	Excess total Br_2 per cent.
1.	16.55	0.07287	18.55	0.33	18.23	0.07274	- 0.20
2.	20.06	0.08830	23.01	0.81	22.22	0.08867	+ 0.40
3.	22.18	0.09765	24.81	0.26	24.56	0.09800	+ 0.37
4.	19.61	0.08634	22.19	0.55	21.65	0.08638	+ 0.05
5.	14.94	0.06578	16.72	0.22	16.50	0.06583	+ 0.08
Mean value of excess total bromine :-							$+0.14 \pm 0.11$ per cent.
Mean error in each determination of excess total bromine:- ± 0.26 per cent.							

(b) Experiments with the aluminium spark in operation.

No.	$\text{Na}_2\text{S}_2\text{O}_3$ Titration c.c.	Normality of free Br_2	AgNO_3 added c.c.	NH_4CNS Titration c.c.	AgNO_3 required c.c.	Normality of total Br_2	Excess total Br_2 per cent. ²
1.	14.11	0.06210	15.91	0.20	15.71	0.06267	+ 0.90
2.	14.39	0.06335	16.35	0.35	16.01	0.06387	+ 0.88
3.	14.44	0.06350	16.53	0.50	16.04	0.06399	+ 0.68
4.	12.65	0.05569	14.19	0.08	14.11	0.05628	+ 1.05
Mean value of excess total bromine:-							$+ 0.88 \pm 0.08$ per cent.
Mean error in each determination of excess total bromine:- ± 0.16 per cent.							

GROUP III.

Normality of sodium thiosulphate solution:- 0.09725
 Normality of silver nitrate solution:- 0.08973

10.00 cc. ammonium thiocyanate are equivalent to:-
 10.89 cc. silver nitrate solution.

(a) 'Blanks'

No.	$\text{Na}_2\text{S}_2\text{O}_3$ Titration c.c.	Normality of free Br_2	AgNO_3 added c.c.	NH_4CNS Titration c.c.	AgNO_3 required c.c.	Normality of total Br_2	Excess total Br_2 per cent.
1.	27.08	0.1054	29.98	0.69	29.22	0.1047	-0.48
2.	19.40	0.07547	21.28	0.29	20.96	0.07523	-0.35
3.*	19.59	0.07619	21.55	0.43	21.08	0.07566	-0.72
4.*	20.98	0.08162	23.08	0.38	22.67	0.08138	-0.30
5.*	19.70	0.07666	21.81	0.55	21.22	0.07616	-0.65
6.*	25.81	0.1004	28.54	0.66	27.82	0.09985	-0.58

Mean value of excess total bromine:- -0.51 ± 0.07 per cent

Mean error in each individual determination of excess
 total bromine:- ± 0.17 per cent.

(b) Experiments with the aluminium spark in operation.

No.	$\text{Na}_2\text{S}_2\text{O}_3$ Titration c.c.	Normality of free Br_2	AgNO_3 added c.c.	NH_4CNS Titration c.c.	AgNO_3 required c.c.	Normality of total Br_2	Excess total Br_2 per cent.
1.	22.72	0.08838	25.68	0.90	24.70	0.08869	+0.32
2.	24.16	0.09400	26.49	0.22	26.23	0.09420	+0.25
3.	22.82	0.08870	25.07	0.22	24.83	0.08912	+0.50
4.*	16.71	0.06502	18.88	0.65	17.17	0.06522	+0.32
5.*	21.18	0.08240	23.79	0.71	23.02	0.08262	+0.28
6.*	26.18	0.1019	29.39	0.83	28.49	0.1023	+0.42

Mean value of excess total bromine:- $+0.35 \pm 0.04$ per cent

Mean error in each individual determination of excess
 total bromine:- ± 0.10 per cent.

N.B. It will be observed that the change of the
 reducing agent from sulphurous acid to hydrazine
 sulphate produces no change in the values for the
 excess total bromine.

The amount of bromine converted into hydrogen bromide by the radiation from the aluminium spark can now be obtained as the difference between the excess total bromine in the 'blanks' and the experiments proper. Thus we obtain, for the percentage by weight of bromine converted into hydrogen bromide:-

Group I:- $(1.07 \pm 0.10) - (0.27 \pm 0.07) = 0.80 \pm 0.17$ per cent.

" II:- $(0.88 \pm 0.08) - (0.14 \pm 0.11) = 0.74 \pm 0.19$ " "

" III:- $(0.35 \pm 0.04) - (-0.51 \pm 0.07) = 0.86 \pm 0.11$ " "

Mean:- 0.8 ± 0.1 per cent.

NOTE ON THE ACCURACY OF THE EXPERIMENTAL METHOD.

The mean error in each individual determination of the excess total bromine varies from 26 in 10,000 to 10 in 10,000, the higher degree of accuracy being obtained in the later experiments (group III).

It was impossible to reduce the error below this, as the analytical method employed involved the following measurements in each determination:-

In the estimation of the free bromine:-

(1) The measurement of a volume of the solution from B_2 by means of a pipette.

(2) The titration with sodium thiosulphate.

In the estimation of the total bromine:-

(1) The measurement of a volume of the solution from B_2 by means of a pipette.

(2) The measurement of the volume of the silver nitrate solution added by means of a burette.

(3) The titration with ammonium thiocyanate.

Since the figures for the excess total bromine were obtained as the difference of the values for the free and total bromine, a mean error x in each of these values will entail a mean error $\sqrt{2} x$ in the figures for the excess total bromine. That is to say, a mean error of 14 in 10,000 in this latter value probably arose from errors of 10 in 10,000 in each of the determinations of the free and total bromine. In actual practice, it was found possible, in standardising the solutions used, to obtain results consistent within 12 in 10,000 for both the sodium thiosulphate and silver nitrate solutions.

Another source of error, however, must be considered here. In the absorption of gases in the bubbler B_2 , since the latter is very efficient, all the hydrogen bromide present will certainly be absorbed; at the commencement of an experiment, the absorption of the bromine will also be complete. However, towards the end of the experiment, when the solution in B_2 contains bromine in moderate concentration (say decinormal), not all the bromine will be dissolved from the gas-stream, since the undissolved hydrogen passing through the liquid will still contain bromine at a partial pressure equal to that of the bromine water in B_2 . Hence, as the absorption of/

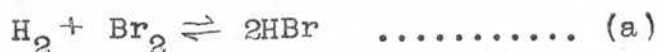
of the bromine is incomplete while that of the hydrogen bromine is complete, the effect of this source of error will be that the calculated percentage of 'excess total bromine' will be higher than that actually present in the gas-stream.

Nevertheless, it can be shown that any error introduced from this source is quite negligible. In every case, the bubbler B₂ was left undisturbed throughout each experiment, and it was noticed that the portion of the solution in that part of the bubbler furthest from the gas-inlet tube N consisted of an extremely dilute solution of bromine - scarcely perceptibly coloured - even at the end of the experiment, the duration of which was about 30-60 minutes. Hence under these conditions, little bromine could be carried away with the hydrogen. Further, if an appreciable amount of bromine were lost in this way, it would be anticipated that the percentage of the excess total bromine would be higher in the experiments of longer duration, when the solution in the bubbler was more concentrated. No trace of this effect is observable in the experimental results, and hence this source of error may be neglected.

THE /

THE INTERPRETATION OF THE EXPERIMENTAL RESULTS.

Undoubtedly the experimental results give qualitative evidence for the formation of hydrogen bromide from its constituent elements under the influence of the radiation from the aluminium spark. However, a careful consideration of the results shows that they yield not only qualitative evidence for the formation of hydrogen bromide, but also give quantitatively the amount of hydrogen bromide present at the equilibrium state. This conclusion is based on the following evidence:- the experiments in group I were all performed with a comparatively feeble spark, while with those in groups II and III the spark was much stronger; actual photometric measurements with the photo-electric cell (by a method described later) showed that the radiation of wave-length $185 \mu\mu$ from the spark in group I was only of $1/8$ th to $1/12$ th its intensity in group II and III. Now, if it be assumed that under the conditions of the experiment, the speeds of both the forward and reverse actions in the equation:-



are proportional to the intensity of illuminations, then it is to be expected that, if the amount of hydrogen bromide formed in the experiments of group I was less than that present at equilibrium under the influence of the aluminium spark, then in the experiments of groups II and III the proportion of hydrogen bromide formed would be somewhat larger, as the /

the increased intensity of the radiation would cause a closer attainment of the equilibrium condition within the same time. Now in actual fact, the amount of hydrogen bromide formed in the experiments of group I, viz., 0.80 ± 0.17 per cent, is exactly the mean of that formed in groups II and III, viz., 0.74 ± 0.19 per cent, and 0.86 ± 0.11 per cent; mean: 0.80 ± 0.16 per cent. Hence, since the amount of hydrogen bromide formed is uninfluenced by a tenfold variation in the intensity of the radiation from the aluminium spark, it must be concluded that the experimental results actually give the proportion of hydrogen bromide in equilibrium with its constituent elements under the experimental conditions prevailing.

This argument assumes that the speed of both forward and reverse actions represented by equation (a) are proportional to the intensity of the light. Now while this is known to be true for the photolysis of hydrogen bromide (Warburg, loc.cit.), the results of Bodenstein and Lütkenmeyer (loc.cit.) show that, in the case of light in the visible spectrum, the velocity of the photosynthesis of hydrogen bromide is proportional to the square root of the intensity of the light. Hence, the assumption made above is not justified. If Bodenstein and Lutkenmeyer's results be assumed for the photosynthesis under consideration, then the position of equilibrium would be affected by the/

the intensity of the illumination. However, as a tenfold variation in the intensity of the spark produces no measurable change in the composition of the gases emerging from the silica spiral, S, it seems justifiable to state that the amount of hydrogen bromide found represents that which exists in equilibrium with its constituent elements under the influence of the radiation from the aluminium spark, at any rate when the latter is of moderate intensity. A further argument showing that the equilibrium condition is reached by the gases during the time (about 3 - 7 minutes) in which they traversed the silica spiral and were exposed to the light from the aluminium spark is to be found in the fact that the proportion of hydrogen bromide formed was noted to be independent of any variation in the speed of the gas-stream through the apparatus.

It is obvious from equation (a) that the ratio of the partial pressures of hydrogen bromide and free bromine in the gas emerging from the apparatus is twice as great as the ratio of the concentrations of these substances in the solution in B_2 , as determined by the analytical method described above. Hence, one concludes that, under the influence of the radiation from the aluminium spark, extending to wavelength $185 \mu\mu$, the system - hydrogen, bromine and hydrogen bromide - is in equilibrium when the partial pressure of/

of the hydrogen bromide is 1.6 ± 0.2 per cent. that of the bromine. The experiments give no information on the effect of the partial pressure of hydrogen (which is perfectly transparent to light of all these wave-lengths) on the position of the equilibrium.

Though it has been proved by these experiments that the total radiation from the aluminium spark causes some formation of hydrogen bromide from its constituent elements, it has yet to be shown that it is actually the light of wave-length shorter than 200μ in this radiation which is effective in producing the photosynthesis, and not the light of longer wave-lengths which is also present.

It was known from the results of Coehn and Stuckardt (*loc.cit.*) that under the influence of the total radiation from the mercury arc extending to 220μ , the equilibrium in the system under consideration lies at complete decomposition of all hydrogen bromide into its constituent elements. Hence, it may be concluded from this that light from the aluminium spark of longer wave-length than 220μ cannot be responsible for the formation of hydrogen bromide observed. Nevertheless, it was decided to confirm this result of Coehn and Stuckardt by repeating the experiments described, but in which the light from the mercury arc was substituted for that from the aluminium spark.

The/

The mercury vapour lamp used for this purpose was made of fused silica, and gave a spectrum containing radiation of reasonable intensity as far as $\lambda = 220\mu\mu$, though the last really strong line was the resonance line, $\lambda = 254\mu\mu$. The following are the experimental results:-

Normality of sodium thiosulphate solution:- 0.1101
 Normality of silver nitrate solution:- 0.09973
 10.00 cc. ammonium thiocyanate solution are equivalent to 9.78 cc. silver nitrate.

$\text{Na}_2\text{S}_2\text{O}_3$ Titration c.c.	Normality of free Br_2	AgNO_3 added c.c.	NH_4CNS Titration c.c.	AgNO_3 required c.c.	Normality of total Br_2	Excess total Br_2 per cent.
(a) 'Blanks'						
15.95	0.07024	18.75	1.14	17.63	0.07032	+0.14
17.36	0.07642	20.26	1.10	19.18	0.07650	+0.11%

(b) Experiments with mercury arc in operation.

18.17	0.07999	21.05	1.04	20.03	0.07990	-0.12
24.31	0.1070	28.03	1.24	26.82	0.1070	-0.05

The error in each individual determination of the excess total bromine may be taken as ± 0.20 per cent, and within these limits the above results give no indication of the formation of any hydrogen bromide by the light from the mercury vapour lamp. Indeed, if anything, one might suspect that the gases emerging from the apparatus contained less hydrogen bromide when the silica spiral was exposed to the light from the/

the mercury arc than when it was in darkness.

It was now decided to investigate whether the radiation from the zinc spark caused any formation of hydrogen bromide. This source of light gives a spectrum extending as far as $202\mu\mu$, and which contains a strong group of four lines between $202\mu\mu$ and $210\mu\mu$; further, it has been shown by Pflüger (loc. cit.) that more than 50 per cent. of the energy radiated consists of light between these wave-lengths. However, experiments with this source of light also gave consistently negative results:-

Normality of sodium thiosulphate solution:- 0.1042

Normality of silver nitrate solution:- 0.09230

10.00 cc. ammonium thiosyanate are equivalent to

10.60 cc. silver nitrate solution.

$\text{Na}_2\text{S}_2\text{O}_3$ Titration c.c.	Normality of free Br_2	AgNO_3 added c.c.	NH_4CNS Titration c.c.	AgNO_3 required c.c.	Normality of total Br_2	Excess total Br_2 per cent.
(a) 'Blanks'						
13.71	0.05715	15.71	0.18	15.52	0.05730	+ 0.28
18.13	0.07559	21.53	0.97	20.50	0.07570	+ 0.16
14.98	0.06245	18.07	1.06	16.95	0.06259	+ 0.23
					Mean	+ 0.22

(b) Experiments with zinc spark in operation.

12.77	0.05324	15.52	1.03	14.43	0.05329	+ 0.10
18.30	0.07630	21.54	0.76	20.74	0.07657	+ 0.38
					Mean	+ 0.24

Hence, it is seen that the observed formation of hydrogen bromide from its constituent elements under the influence of the aluminium spark cannot be/

be attributed to radiation of longer wave-length than $202 \mu\mu$. In the aluminium spark there is present a considerable amount of radiation of shorter wave-length than this, viz., lines at $199 \mu\mu$ and $193 \mu\mu$, and a very strong group at $185 \mu\mu$. Hence the formation of the hydrogen bromide must be attributed to radiation of these wave-lengths. Further, since it is to be expected that the absorption coefficient of bromine increases with decreasing wave-length, and since the group of lines at $185 \mu\mu$ is at least four times the intensity of the other two lines under consideration, it seems reasonable to attribute the formation of the hydrogen bromide to the effect of the radiation of wave-length $185 \mu\mu$ present in the light from the aluminium spark.

PART II.THE MEASUREMENT OF THE COEFFICIENT OF ABSORPTION OF
BROMINE BETWEEN 254 $\mu\mu$ AND 185 $\mu\mu$.

The results of Living and Dewar (collected works) and also the photographs of Coehn and Stuckardt (loc. cit.) seem to indicate that bromine possesses a strong absorption band in the far ultraviolet, becoming appreciably intense at about 240 $\mu\mu$, and increasing rapidly with decreasing wave-length. In fact, it was the belief in the existence of this strong absorption in the far ultraviolet that led to the experiments on the formation of hydrogen bromide from its constituent elements when exposed to light from the aluminium spark.

However, when the spectrum of the light from the aluminium spark was photographed through a column of bromine vapour 8 cm. long and at a pressure of about 120 mm., the absorption in the far ultraviolet did not seem to be great, indeed it was very slight compared with that in the violet of the spectrum, near 420 $\mu\mu$. No appreciable diminution in the intensity of the ultraviolet spectral lines was noticed except in the case of the group at 185 $\mu\mu$, which was somewhat enfeebled, although it could not be said that the absorption was strong even at this wave-length.

In view of these facts, it was decided to make a series of quantitative measurements on the coefficient/

coefficient of absorption of bromine for the spectral range $254\mu\mu$ - $185\mu\mu$; it was impossible to push measurements to shorter wave-lengths than this limit with the ordinary quartz apparatus of the laboratory.

The principle adopted for these absorption measurements was the following. A cell constructed of transparent fused silica and possessing two parallel plane faces was placed between a suitable source of light and the slit of a quartz spectroscope. The intensity of a given spectral line, or group of lines close together, in the light emerging from the spectroscope was measured both with the cell evacuated and also when filled with the bromine vapour, the radiation from the source of light being maintained constant throughout. In this way, the coefficient of absorption of bromine for light of a particular wave-length could be determined from the diminution of intensity of light of that wave-length which took place when the bromine was introduced into the cell.

The silica cell was provided with a side-tube. Previous to performing the absorption measurements, this was connected to an appropriate glass apparatus by means of a ground joint, sealed externally by means of paraffin wax. A few drops of pure bromine were thus introduced into the cell by distillation in vacuo, and the side-tube was then sealed off about 10 cm. from the main body of the cell, so that the latter/

latter then contained no gas other than bromine. To remove all bromine from the cell, it was necessary merely to immerse the side-tube in liquid air, as at that temperature (-186°C) the vapour pressure of bromine is immeasurably small. Again, by immersing the side-tube in a bath at a known temperature (below room temperature), the cell became filled with bromine vapour at a pressure equal to the vapour pressure of bromine at that temperature. This procedure is a slight modification of that used by Ribaud (Ann. Physique, 12, 107; 1919) for his measurements on the coefficient of absorption of bromine in the violet region.

It was then necessary to devise a suitable method for measuring the intensity of a given spectral line in the light emerging from the spectroscope. It was first proposed to use a selenium cell for this purpose, and to measure the change of the resistance of the latter caused by the radiation falling upon it. However, it was found impossible to obtain satisfactory results by this method, though it seems probable that with a sufficiently experienced technique the selenium cell would furnish the best means of measuring the intensity of light of very short wavelength.

Hence it was resolved to employ a photoelectric instead of a selenium cell for the purpose of measuring the/

the intensity of the light. Unfortunately, all types of photoelectric cells are most sensitive to light of considerably longer wave-length than $200\ \mu\mu$, and beyond the position of maximum sensitivity the latter falls off rapidly with decreasing wave-length.

Thus with a potassium cell the sensitivity is at a maximum at $\lambda = 440\ \mu\mu$, and diminishes almost to zero at $250\ \mu\mu$, while with rubidium and caesium cells the region of sensitivity lies in still longer wave-lengths. With a sodium cell, the point of greatest sensitivity is at $\lambda = 340\ \mu\mu$, and the cell possesses some sensitivity to light of wave-length as short as $185\ \mu\mu$. A lithium cell would doubtless be even more useful for measurements on light of very short wave-length, but attempts to construct this latter type of cell have, up till now, met with no success. Therefore, a sodium photoelectric cell with quartz windows (as supplied by Hilger) was adopted for the measurements on the intensity of the light.

Attempts were first made to magnify the photoelectric current from the cell by means of the valve amplifier described by Wynn-Williams (Proc. Camb. Phil. Soc., 23, 810; 1927), and to make use of a Broca galvanometer for measurements on this increased current. However, good results could not be obtained by this method, chiefly because of disturbing currents set/

set up in the valve-amplifier, which caused great unsteadiness in the Zero position of the galvanometer. No doubt the sparks used as the source of light contributed greatly to the lack of success with this method.

Finally, the photo-electric cell was used in conjunction with a Lindemann electrometer as shown in fig. 2.

A difference of potential of 100 volts was maintained between the anode and cathode of the photo-electric cell by connecting the cathode to the negative terminal of a battery giving 100 volts, the positive pole of which was earthed. The anode of the photo-electric cell was earthed through a high resistance 'leak' of about 10^{12} ohms, consisting of a narrow tube filled with a mixture of anhydrous alcohol and xylene. The anode was also connected to the needle of the Lindemann electrometer. With this arrangement, the potential between the electrometer-needle and earth, i.e. the potential across the high resistance 'leak', is proportional to the current flowing through the photoelectric cell, and hence the electrometer acts as a sensitive galvanometer in measuring this current. The quadrants of the electrometer were adjusted to suitable potentials by moving the earthing point on the potential divider. The deflections of the needle were observed by means of a microscope with/

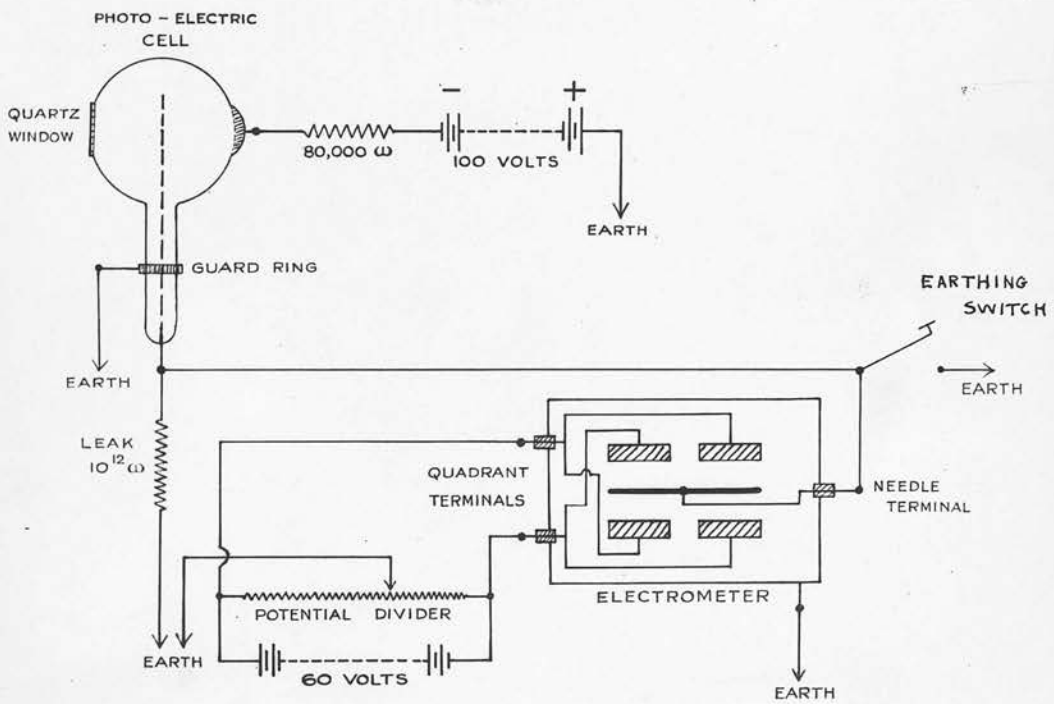


Fig. 2.

with eyepiece scale. (F.A. & A.F. Lindemann and Keeley, Phil. Mag., 47; 1924).

A slit of width about 0.2 cm. was placed in the focal plane of the spectroscope, so as to allow only light of the desired wave-length to enter the photoelectric cell. It was assumed that the photoelectric current, and hence the deflections of the electrometer-needle, were, other things being equal, proportional to the intensity of the light entering the photoelectric cell.

The coefficient of absorption of bromine was measured for the mercury line, $\lambda = 254 \mu\mu$, using the mercury vapour arc as a source of light, and for the zinc line, $\lambda = 206 \mu\mu$, and the aluminium doublet, $\lambda = 185 \mu\mu$, using the appropriate spark as the source of light. To prevent electro-static disturbance to the electrometer, the spark was surrounded by an earthed metallic box, in which a hole was cut opposite the slit of the spectroscope.

Two silica absorption cells were employed, both having been previously evacuated and filled with bromine as described above. In the one case the length of the absorbing column (i.e., the distance internally between the two parallel faces) was 1.07 cm., and in the other 8.0 cm.

The coefficient of specific absorption was calculated thus:- if D_0 and D_1 be the deflections of/

of the needle of the electrometer, as measured in the units of the eyepiece scale, with the absorption cell respectively empty and containing bromine at a pressure of p mm. and absolute temperature T° , then for the coefficient of specific absorption of bromine ($k_\lambda^{p;T}$) at that pressure the temperature, and for the wavelength (λ) of the light used, we have:-

$$k_\lambda^{p;T} = 2.3/l (\log_{10} D_0 - \log_{10} D_1)$$

where l is the length of the absorbing column of bromine vapour.

Further, if M_λ is the coefficient of molecular absorption of bromine at N.T.P. for wave-length λ , we get:-

$$M = \frac{22400 \times 760 \times T}{p \times 273} k_\lambda^{p;T}$$

If it be assumed that the bromine vapour obeys the gas laws, and Beer's law of absorption, this quantity should depend solely on λ , and be independent of pressure and temperature. It is known, however that few gases obey Beer's law strictly (Warburg, loc.cit.) and it seems unlikely also that the bromine vapour follows the gas-laws closely. In this connection, moreover, it has been shown by Ribaud (loc.cit.) that, in the case of the absorption band of bromine in the violet, the position of maximum absorption varies with the temperature of the bromine. This effect probably occurs also with the ultra-violet absorption band, /

band, but the error introduced from this source is negligible for the small range of temperature (15°) used in the experiments. In any case, the accuracy of the experiments cannot be estimated at more than ± 10 per cent, owing chiefly to fluctuations in the source of light; this is particularly true in the case of the measurements on the zinc and aluminium lines, where a spark was employed as a source of light.

In measuring the deflections of the electrometer-needle, the following procedure was adopted. The photoelectric cell was provided with a shutter in front of the quartz window, and this was opened and light from the appropriate spectral line (or group of lines) was allowed to enter the cell. After 45 seconds exposure to the light, the deflection of the needle was noted, as it was found that this length of exposure was sufficient to allow the deflection to reach its final value. The shutter was then closed, and the electrometer needle brought back to the position of zero deflection by closing the 'earthing switch' (see fig.2) for about 30 seconds. The above procedure could then be repeated. The values adopted for D_0 and D_1 were the mean of several (usually six) independent readings of the deflections of the electrometer needle.

Results. /

Results.

λ	l cm.	D_0	t °C	p mm.	D_1	$k_\lambda^{p;T}$	M_λ
254	1.07	35.5	15	136	34.8	0.018	0.238×10^4
206	1.07	11.6	14	130	10.7	0.075	1.06×10^4
206	1.07	65	0	66	62.3	0.039	1.07×10^4
185	1.07	75	0	66	67	0.105	2.87×10^4
185	1.07	69	12.5	121	55	0.211	3.15×10^4
185	8.0	21	0	66	9	0.105	2.87×10^4

N.B. The column t gives the temperature of the bath in which the side-tube of the silica cell was immersed while measuring D_1 , and the values of p are the vapour pressures of bromine at those temperatures, as given by Ribaud (loc.cit.). The temperature, T , of the bromine vapour in the main body of the cell, was that of the room, viz., 16°C or 289° abs.

Adopting the mean values for the coefficient of molecular absorption we get:-

$$M_{\lambda=254} = 0.24 \times 10^4$$

$$M_{\lambda=206} = 1.1 \times 10^4$$

$$M_{\lambda=185} = 3.0 \times 10^4$$

For the sake of comparison, it is interesting to note that for the mercury vapour line at $\lambda = 436 \mu\mu$ which is near the point of maximum absorption ($\lambda = 420 \mu\mu$) for bromine in the violet, it was found by a photographic method that the coefficient of molecular absorption is about 5×10^5 . Hence, even at the short wave-length of $185 \mu\mu$, the absorption by bromine is small compared to that which it exerts in the violet. That a deeply coloured gas like bromine should/

should be so transparent in the far ultraviolet is somewhat remarkable, and it should be observed in this connection that the absorption spectra photographs of Coehn and Stuckardt (loc.cit.) and the results of Living and Dewar (loc.cit.) are somewhat misleading, as they seem to show that bromine is much more opaque in the further ultraviolet region. It would be interesting to know if the absorption by iodine in the region $250\mu\mu$ - $185\mu\mu$ is really as strong as is indicated by Coehn and Stuckardt, or if the absorption is comparatively slight, like the corresponding absorption band of bromine. However, in view of the strong fluorescent spectrum emitted by iodine vapour when exposed to the light from the aluminium spark, it seems likely that iodine is very opaque at the wave-length $185\mu\mu$. Also the emission spectrum of iodine shows a series of lines beginning at $206\mu\mu$, (Ludlam and West, loc.cit.) and hence this gas probably absorbs strongly at this wave-length; indeed the unpublished work of these authors demonstrates this fact directly.

Incidentally, it was found in the course of these measurements that the transparency of different specimens of fused silica varied greatly for light of wave-length $185\mu\mu$, and that the degree of transparency of a specimen was roughly inversely proportional to the amount of fluorescence exhibited on exposure/



exposure to the light. One of the absorption cells used cut off about 75 per cent of the incident light, and the other nearly 90 per cent; in each case the combined thickness of the two parallel faces was about 0.4 cm. Since the silica spiral used in the equilibrium experiments (Part I) was of thin-walled tubing (0.5 mm.) and fluoresced only very slightly when illuminated by the aluminium spark, it was concluded that it was fairly transparent to light of wave-length $185\mu\mu$.

The main source of error, or even of completely spurious results, in these absorption measurements might be the presence of scattered radiation of heterogenous wave-length in the light emerging from the spectroscope. This scattered light was liable to be produced by reflections from the edges of the lenses used in the optical system of the spectroscope. Hence an experiment was performed to investigate how much of the deflection of the electrometer was due to light of wave-length $185\mu\mu$ entering the cell, and how much was due to 'false' light of heterogenous wave-length entering along with it. The deflections of the electrometer-needle by the photoelectric current, when the aluminium doublet at $\lambda = 185\mu\mu$ entered the photoelectric cell, were measured with and without a thin slice of calcspar interposed between the source of light and the slit of the spectroscope. Calcspars cuts/

cuts off all wave-lengths shorter than $208\mu\mu$, but is perfectly transparent to all longer wave-lengths, hence any deflection apparently produced by the aluminium doublet $\lambda = 185\mu\mu$ with this substance interposed must be due to the 'false' light entering the photoelectric cell. In this way it was found that the interposing of the calcspar cut down the deflection from 70 to 0.5 scale-divisions, and hence it is seen that errors due to the presence of scattered light in the spectroscope are entirely negligible. This precautionary experiment was essential, since the sodium cell is extremely sensitive to light in the violet and near ultra-violet regions of the spectrum, and bromine absorbs strongly light of this wavelength.

The results of the absorption measurements show that the absorption coefficient of bromine rises very slowly with decreasing wave-length in the range $254\mu\mu - 185\mu\mu$. In fact, this ultra-violet absorption band differs strongly from that of the same element in the visible spectrum, which rises to a sharp maximum at $\lambda = 420\mu\mu$. The ultraviolet absorption of bromine resembles somewhat that of iodine in the ultraviolet, as, according to the work of Coehn and Stuckardt, the absorption coefficient of this element rises slowly on passing from $350\mu\mu$ to $220\mu\mu$, at which latter wave-length the gas is practically opaque.

DISCUSSION OF THE RELATIONSHIP BETWEEN THE RESULTS
OF THE EQUILIBRIUM EXPERIMENTS AND THOSE OF THE
ABSORPTION MEASUREMENTS.

Coehn and Stuckardt (loc.cit.) came to the conclusion that the absorption bands of the halogens and their hydrides might be divided into two classes. The first type comprises those bands in which the absorption coefficient rises rapidly with decreasing wave-length, and to this class belong the absorption bands of the halogen hydrides, and those of the halogens in the visible. The other type comprises those bands in which the opacity of the gas increases but slowly and steadily with decreasing wave-length, and as examples of absorption bands of this type we have those of bromine and iodine in the further ultraviolet. Now Coehn and Stuckardt concluded that absorption of light by a band of the first class meant that the energy absorbed was converted into chemical energy by 'activation' of the molecules of the absorbent, while in the case of a band of the second class, the absorbed radiation was converted into 'thermal' energy, by increasing the translational energy of the molecules of the absorbent. Hence one would expect that in the first case, under appropriate circumstances, the absorption of light would produce chemical change, while/

while in the second case, little, if any, chemical change would tend to occur. Coehn and Stuckardt use this reasoning to explain the absence of any trace of formation of hydrogen bromide in their experiments, in which a mixture of hydrogen and bromine were exposed to the full radiation of the mercury arc (extending to $\lambda = 220 \mu\mu$), by assuming that light of this latter wave-length absorbed by the bromine is converted into thermal and not chemical energy. However, it is difficult to reconcile the above argument with the existence at equilibrium of 7.5 per cent hydrogen iodide under the same experimental conditions, since the ultraviolet absorption band of iodine undoubtedly belongs to the second class. It seems more logical to conclude that there is no sharp division between the two types of absorption band, though probably in the first case more of the energy absorbed goes to 'activate' the molecules of the absorbent than in the second case. The fact that no formation of hydrogen bromide takes place under the influence of radiation from the mercury arc is easily explained, since the absorption of bromine for $\lambda = 220 \mu\mu$ has been shown to be very much less than that given by Coehn and Stuckardt. If it be assumed that the system - hydrogen, bromine and hydrogen bromide - is in equilibrium when as much energy is absorbed from the radiation by the hydrogen bromide as by the bromine, /

bromine, then it is easy to see that this condition is satisfied if the partial pressure of hydrogen bromide is extremely small compared to that of bromine. Thus for the zinc line, $\lambda = 209 \mu\mu$, Warburg (loc.cit.) found that the coefficient of molecular absorption of hydrogen bromide is 154×10^4 , while the absorption measurements just described have shown that that of bromine at $\lambda = 206 \mu\mu$ is 1.1×10^4 ; hence at equilibrium the partial pressure of the hydrogen bromide would be 0.66 per cent that of the bromine. The zinc spark furnishes strong radiation at this wave-length, but the equilibrium experiments described with this source of light are not sufficiently delicate to detect the presence of such a small percentage of hydrogen bromide as this, especially since the analytical method described would yield as a result half the above figure, i.e. 0.33 per cent. With the meagre experimental data available this figure lies just within the limits of experimental accuracy, and it is not entirely excluded by the negative results of the experiments with this source of illumination.

It is interesting to calculate the position of equilibrium in the system under the influence of radiation from the aluminium spark of wave-length $185 \mu\mu$, assuming, as before, that equilibrium is reached when the energy absorbed by the hydrogen bromide is equal to that absorbed by the bromine. Extrapolating/

Extrapolating from Warburg's figures for $\lambda = 253 \mu\mu$ and $\lambda = 209 \mu\mu$, we may take as a probable value for the coefficient of molecular absorption of hydrogen bromide for $\lambda = 185 \mu\mu$ the value 200×10^4 , while, since that of bromine at this wave-length is 3.0×10^4 , at equilibrium the partial pressure of the hydrogen bromide will be 1.5 per cent that of the bromine. This value agrees sufficiently well with that obtained in the case of the equilibrium experiments with the aluminium spark, viz., 1.6 ± 0.2 per cent.

This method of calculation of the position of equilibrium in the system under the influence of radiation of a particular wave-length, from the coefficient of absorption of the components of the system, involves simplifications which are based on preliminary assumptions which are not strictly justified. Thus, it is assumed that all the energy absorbed from the radiation is utilized in producing chemical change, or, alternatively, the same fraction of it is used in both the forward and the reverse reactions. Again, it is assumed that the absorption of one quantum of energy by a molecule of hydrogen bromide would lead to the formation of as many molecules of bromine as would be reconverted into hydrogen bromide by the absorption of a quantum of energy by a molecule of bromine. Since it is known (Warburg loc.cit.) that with hydrogen bromide the absorption of one quantum leads/

leads ultimately to the decomposition of two molecules of this substance, that is, the formation of one molecule of bromine together with one of hydrogen, this assumption stipulates that the absorption of one quantum of light by a molecule of bromine will give rise to two molecules of hydrogen bromide.

This is not in accordance with the work of Bodenstein and Lütkemeyer (loc.cit.) who showed that, in the case of visible light, the amount of hydrogen bromide formed was proportional to the square root of the quantity of energy absorbed by the bromine. However, since the 'Konvergenzstelle' of bromine lies at

$\lambda = 510 \mu\mu$, it is seen that visible light produces just sufficient energy to bring about the primary reaction in the photosynthesis of hydrogen bromide, viz., the dissociation of the bromine molecule into atoms, while with ultraviolet light of wave-length $185 \mu\mu$ a large excess of energy is present. Hence it is quite possible that the mechanism of the reaction will be different in the two cases, and that with light of very short wave-length the quantum of energy will convert one molecule of bromine into two of hydrogen bromide; in this case, the reaction will resemble that of bromine on hexahydrobenzene (Nernst and Pusch, loc.cit.; Noddack, loc.cit). In favour of this, and as a further justification of this preliminary assumption, there is the fact that, in the/

the equilibrium experiments with the aluminium spark, it was found that the position of equilibrium was unaffected by the intensity of the radiation, which would seem to show that the square-root law for the velocity of photosynthesis of hydrogen bromide does not hold in the case of light of very short wavelength.

Hence, in connection with these two assumptions, it may be said that, although neither may be fully justified, the calculation based thereon is not without interest. It should be noted that divergences from the one assumption may be partly neutralized by divergences from the other.

Finally in this connection it must be again emphasized that in the equilibrium experiments we are not dealing with ultraviolet light of very short wavelength per se, but with the complete zinc or aluminium spectrum so far as it can be transmitted through fused silica. The experiments with the mercury vapour arc and the zinc spark show that radiation consisting of wavelengths as far as $\lambda = 202 \mu\mu$ does not produce any formation of hydrogen bromide and hence the formation of this substance under the influence of the aluminium spark can only be attributed to the radiation of shorter wavelength present in the light from this source. However, it is known that the full radiation of the mercury arc rapidly /

rapidly produces complete decomposition of hydrogen bromide. Hence, in the state of equilibrium reached under the influence of the radiation from the aluminium spark, that of longer wave-length than $202 \mu\mu$ must be aiding the decomposition of the hydrogen bromide present and consequently it is probable, that, under the influence of purely monochromatic radiation of wave-length $185 \mu\mu$, somewhat more hydrogen bromide would be present than when the system is exposed to the full radiation from the aluminium spark. It would be extremely desirable to investigate the equilibrium in the system under the influence of such monochromatic light, were not the difficulties of producing such illumination, in sufficient intensity, extremely great.

CONCLUSION.

The photochemistry of the formation and decomposition of hydrogen bromide has now been fairly fully investigated. Thus we have the work of Bodenstein and Lütkemeyer on the mechanism of the formation of this substance under the action of light in the visible spectrum, together with the same authors' researches on the same action taking place thermally in the dark. Also there exists the work of Warburg, who showed that the decomposition of hydrogen bromide by ultraviolet light followed Einstein's law of photochemical equivalence. Along with these researches on the separate reactions of formation and decomposition of the hydrogen bromide, we have the work of Coehn and Stuckardt investigating the final condition of equilibrium reached when either hydrogen bromide or its constituent elements are exposed to the action of light of different wave-lengths.

The research just described is an extension of that of Coehn and Stuckardt. The facts learned from it may be summarised thus:-

(1) Hydrogen and bromine combine to a small extent when exposed to the light from the aluminium spark, which radiates strongly at $\lambda = 185 \mu\mu$. At equilibrium under these conditions, the partial pressure of the hydrogen bromide is about 1.4 to 1.8 per cent. that of the bromine.

(2) The absorption coefficient of bromine increases slowly with decreasing wave-length for wave-lengths shorter than $254 \mu\mu$, but the gas is still very transparent even at $185 \mu\mu$.

(3) Theoretical considerations, especially the analogy with Coehn and Stuckardt's results obtained with hydrogen iodide, lead one to anticipate that a small amount of formation of hydrogen bromide from its constituent elements must take place under the influence of radiation of wave-length $185 \mu\mu$. Also a consideration of the values of the absorption coefficients of bromine and hydrogen bromide for light of this wave-length suggests that at equilibrium the amount of hydrogen bromide formed would be about that actually found by experiment.

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