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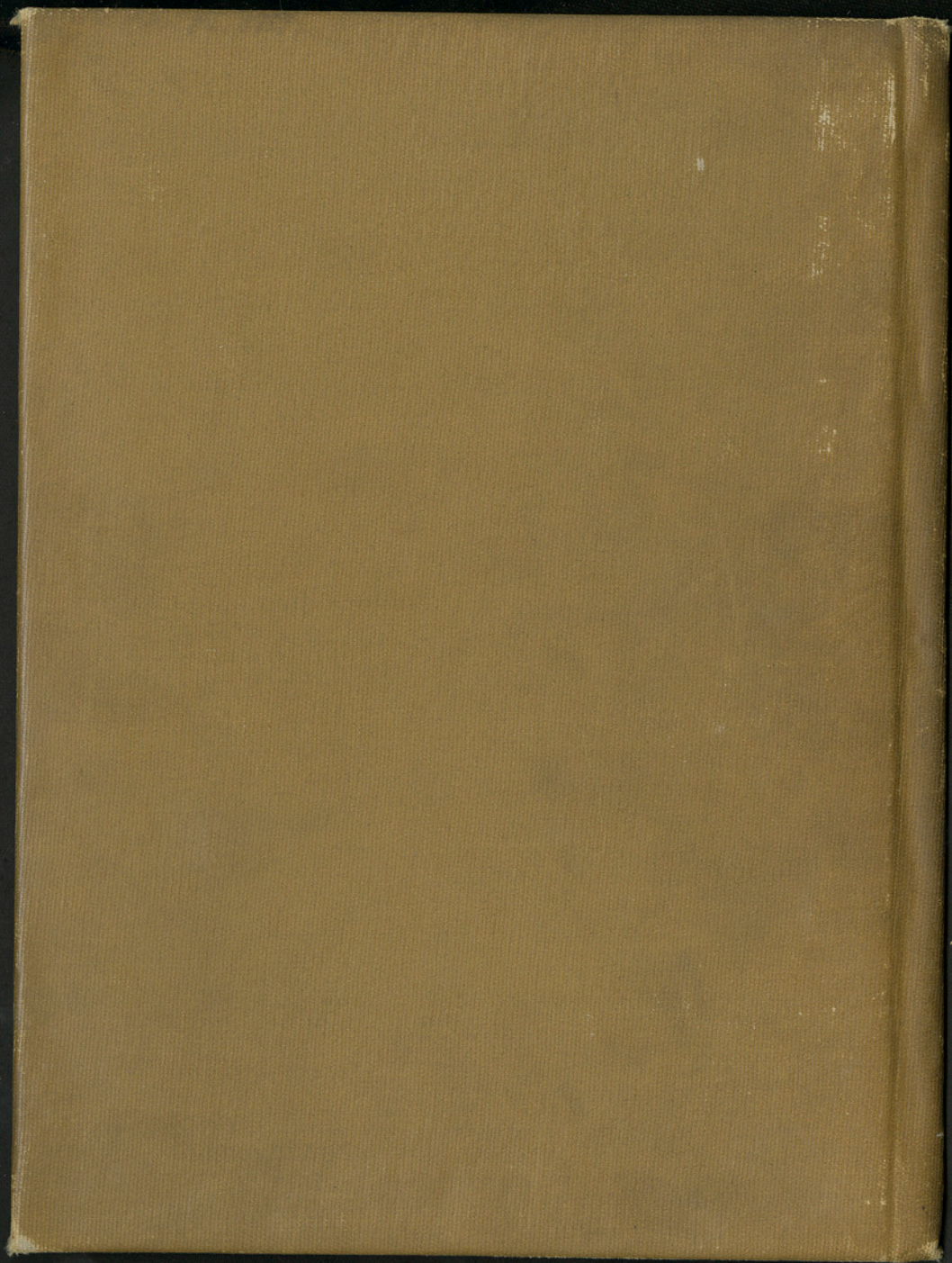
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MECHANISM OF THE  
PHOTOCHEMICAL COMBUSTION  
OF HYDROGEN AND CHLORINE

BY  
ALLAN C. G. MITCHELL







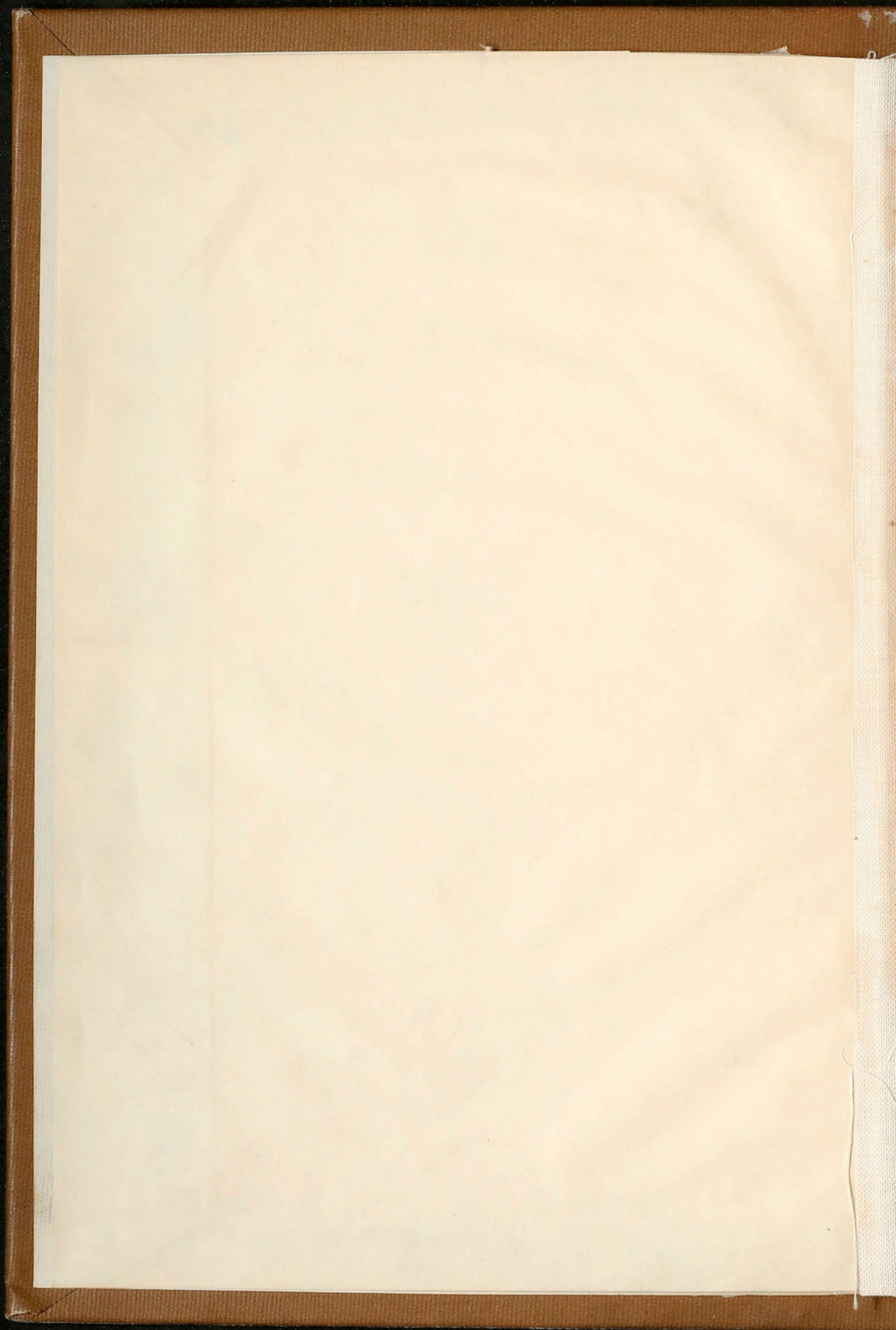


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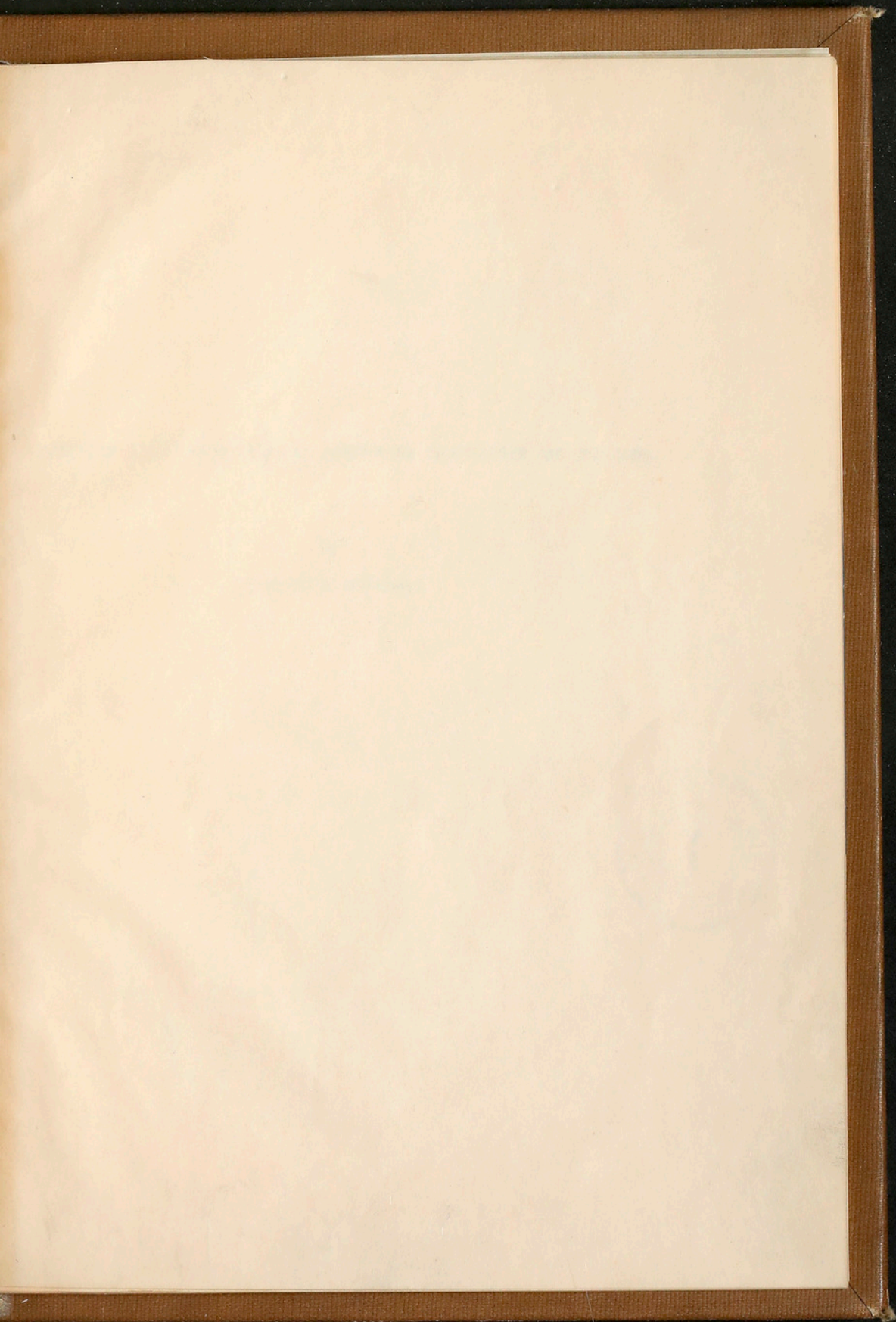


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Allan C. G. Mitchell





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MECHANISM OF THE PHOTOCHEMICAL COMBUSTION OF HYDROGEN AND CHLORINE.

A Thesis presented to the Academic Faculty of the  
University of Virginia in candidacy for the degree  
of Master of Science.

by

Allan C. W. Mitchell



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## MECHANISM OF THE PHOTOCHEMICAL COMBUSTION OF HYDROGEN AND CHLORINE.

### I. Concerning Light.

Light is the result of the vibrations of charged particles called radiators or vibraters, which may be either atoms or electrons. These vibrations cause the emission of electro-magnetic waves, all travelling with the same speed ( $3 \times 10^{10}$  cm. per sec.). The waves may be all of the same frequency, or, as is more frequently the case, of a number of different frequencies. If the waves are all of the same frequency we have what is known as monochromatic light, which is characterized by having a definite color. If, however, there are a number of frequencies emitted the light will appear white and on being analysed by a spectroscope will give rise to a spectrum.

In order that the vibrations of the charged particles may continue for any length of time energy must be supplied. When this energy is supplied in the form of heat, the radiation is called "temperature radiation". Any substance heated to a sufficiently high temperature must give rise to such temperature radiation. Radiation which is not the result of high temperatures but of some chemical change is called "luminescence". This is the case in the flame of a Bunsen burner or of burning  $CS_2$ .

The frequencies which go to make up the "visible spectrum" are only a small part of all the possible frequencies which may be given out in any radiation process. In addition to the visible spectrum there is the infra-red region which is made up of the waves of slower frequency, heat and electric waves, and the ultra-violet region which is made up of the higher frequencies, giving photographic light and X-rays. As lines of the spectrum are usually given in terms of wave-lengths instead of frequencies, we will use this term in defining the limits of the visible spectrum, remembering the familiar relation



1. The energy of the incident light

Let us first consider the emission of electrons from a metal surface. The energy of the incident light is  $h\nu$ , where  $h$  is Planck's constant and  $\nu$  is the frequency of the light. The energy of the emitted electron is  $h\nu - \phi$ , where  $\phi$  is the work function of the metal. The maximum kinetic energy of the emitted electron is  $h\nu - \phi$ . The energy of the incident light is  $h\nu$ . The energy of the emitted electron is  $h\nu - \phi$ . The energy of the incident light is  $h\nu$ . The energy of the emitted electron is  $h\nu - \phi$ .

In order that the emission of the electron should be possible, the energy of the incident light must be greater than the work function of the metal. The energy of the incident light is  $h\nu$ . The energy of the emitted electron is  $h\nu - \phi$ . The energy of the incident light is  $h\nu$ . The energy of the emitted electron is  $h\nu - \phi$ .

The frequency of the incident light must be greater than the threshold frequency of the metal. The energy of the incident light is  $h\nu$ . The energy of the emitted electron is  $h\nu - \phi$ . The energy of the incident light is  $h\nu$ . The energy of the emitted electron is  $h\nu - \phi$ .



$$c = \nu \lambda$$

where  $c$  is the velocity of light,  $\lambda$  is the wave length, and  $\nu$  the frequency. The visible spectrum stretches from  $\lambda 4000$  to  $\lambda 8500$  angstrom units ( $10^{-8}$  cms), the long wave lengths corresponding to the red end of the spectrum and the short to the violet. In this paper we will have to consider only the visible spectrum, with perhaps slight mention of the ultra-violet.

Kirchhoff's first Law states that light of any given wave length emitted by a gaseous body can also be absorbed by that body at a lower temperature. The emission lines are bright, while the absorption lines appear as dark lines in the spectrum. The Second Kirchhoff Law states that the ratio of the emissive power of a body to the absorptive power of that body is a function of the temperature only. This is symbolized by the equation,  $E/A$  constant.

The amount of light absorbed by a given gas is proportional to the thickness of the layer through which it passes.<sup>1</sup> Hence it follows that the change in intensity  $dI$ , with the thickness  $dl$ , at a point  $l$ , where the intensity is  $I$  is given by the relation

$$- dI/dl = kI$$

This is known as Lambert's law, On integrating we have

$$I = I_0 e^{-kl}$$

where  $I_0$  is the intensity of the light before entering the absorbing medium.

In the case of solutions we have a similar law known as Beer's law, involving the concentration. If  $c$  is the concentration of colored material, we have

$$- dI/dl = kcl$$

$$\text{or } I = I_0 e^{-kcl}$$

Having derived these laws we are now in a position to discuss the absorption

1. W. C. McC. Lewis- Systems of Physical Chemistry, vol II.

2. J. Pletáikow- Lehrbuch der Photochemie.



above is the intensity of light,  $I$ , in the case of a plane wave, and  $I_0$  is the intensity of light in the case of a plane wave, and  $I_0$  is the intensity of light in the case of a plane wave.

The ratio of the intensity of light,  $I$ , to the intensity of light,  $I_0$ , is the ratio of the intensity of light,  $I$ , to the intensity of light,  $I_0$ , and is the ratio of the intensity of light,  $I$ , to the intensity of light,  $I_0$ .

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spectrum of chlorine.

A detailed study of the absorption spectrum of chlorine has been made by Mrs. Laird. A fifteen-foot Rowland grating was used as a spectroscope and the lines were measured photographically. Both sunlight and an electric arc were used as sources of light. One meter of chlorine at atmospheric pressure was used. The absorption spectrum was found to consist of lines beginning at  $\lambda 4799$  A. U. and extending to  $\lambda 5350$ . The first lines in the blue are very faint, as are also these in the yellow above  $\lambda 5200$ . These of maximum intensity lie nearer to the blue than to the yellow. There is also general absorption in the violet. The effect of increasing the pressure on the line spectrum was to increase the intensity of the lines. New lines further up into the yellow appeared with increase of intensity and the general absorption advanced up to  $\lambda 4990$ . For our purposes, then, we may consider the absorption spectrum of chlorine to be made up of lines for the most part in the blue and the green.

Among the phenomena exhibited by light which have special bearing on this paper are the so-called Zeeman and Stark effects. For a full explanation of these phenomena one must dive deep into the mathematical theory of atomic structure and this is beyond the scope of this paper.<sup>2</sup> However, it is necessary to give a brief discussion of the details of the Zeeman and Stark effects and to indicate something of the nature of their cause.

Consider the effect of a magnetic field on the motions of a charged body. It can be shown<sup>3</sup> that the light emitted from an electron vibrating in the absence of a field with a frequency  $\nu_0$  would be changed by the presence of a magnetic field of intensity  $H$  into three components of frequency  $\nu_0 + d\nu$ ,  $\nu_0$ ,

$\nu_0 - d\nu$ , where

$$d\nu = \frac{H e}{4\pi m c}$$

1. Astrophysical Journal XIV, 85, 1901

2. cf. A. Sommerfeld- Atombau und Spektrallinien

3. N. R. Campbell- Modern Electrical Theory, Chap XV



A detailed study of the electrical properties of dielectric materials is presented in this paper. The authors discuss the various factors which influence the dielectric constant and loss tangent of these materials. They show that the dielectric constant is a function of the frequency of the applied field, and that the loss tangent is a function of the frequency and the dielectric constant. The authors also discuss the effect of temperature and humidity on the dielectric properties of these materials.

The authors also discuss the effect of the dielectric constant on the propagation of electromagnetic waves. They show that the dielectric constant of a material determines the velocity of propagation of electromagnetic waves through the material. They also discuss the effect of the dielectric constant on the reflection and refraction of electromagnetic waves at the interface between two dielectric materials.

1. Introduction  
2. Dielectric Properties of Dielectric Materials  
3. Effect of Frequency on Dielectric Properties  
4. Effect of Temperature and Humidity on Dielectric Properties  
5. Propagation of Electromagnetic Waves in Dielectric Materials  
6. Reflection and Refraction of Electromagnetic Waves at Dielectric Interfaces  
7. Conclusion



If the light is observed along the direction of the field, only the components  $\sqrt{I_x^2 + I_y^2}$  should be observed and they should be circularly polarised in opposite senses; if the light is observed at right angles to the field, all three components should be observed and should be plane polarised. From the above equation we see that the greater the strength of the magnetic field, H, the greater the frequency difference of the components.

Zeeman first examined a flame colored with sodium and placed between the poles of an electromagnet but was unable to detect any change in the lines of the spectrum. Later, by placing the flame between the poles of a powerful Ruhmkorff magnet and analysing the light with a ten-foot Rowland grating, a shift in the lines was detected in the following manner. A micrometer eye-piece was focussed on the D lines of the sodium flame. When the current was put on the distance between the lines was seen to widen; and, conversely, when the current was shut off the lines returned to their former position. In later works<sup>2</sup> by Zeeman and others doublets and triplets have been found in the spectrum of zinc, cadmium, copper, and other metals. Also it has been shown by Zeeman that when the spectrum is obtained in the direction of the field the doublets are <sup>each</sup> polarised in ~~the~~ opposite direction<sup>5</sup>. These experiments were performed on absorption as well as <sup>on</sup> emission spectra. The fields used varied from 30,000 to 50,000 C. G. S. units. It will readily be seen that such strong electro-magnetic fields are hard to obtain and especially if they are spread over any large area.

Let us now give our consideration to the other phenomenon, the Stark effect. This has to do with the effect of an electrostatic field on spectral lines and can only be explained on the basis of the Bohr atom with its electrons revolving in circles and ellipses.<sup>3</sup>

1. Verhandelingen van Dr. P. Zeeman over Magneto-Optische Verschijnselen.
2. E. C. C. Baly- Spectroscopy, Chap XVI
3. A. Sommerfeld- Atombau und Spektrallinien







J. Stark, in 1913, experimented on the lines of the Balmer series for hydrogen, and later on a number of other elements, He, Li, etc., The experimental difficulties were very great. The object was to subject the hydrogen atoms during their emission to a powerful electric field of about 100,000 volts per cm. Since the Geissler tubes in which the hydrogen lines were produced were good conductors a field could not be maintained in them. However, by using a canal ray tube and putting a field directly behind the cathode the desired effect was obtained. The following is a summary of the experimental results obtained by Stark as given by Sommerfeld:

1. Every Balmer line becomes split up into a number of components.
2. The number of components increases with the series number of the line.
3. The components are linearly polarised when viewed transversally (transverse), being polarised partly parallel to the field (p-components) and partly perpendicularly to it (s-components).
4. When viewed longitudinally (longitudinal effect) the p-components are invisible and the s-components are unpolarised.
5. The resolution (the distance between components) increases proportionally with the field.

Since, in this paper we have to do with the longitudinal effect only, the application of an electric field would amount merely to the breaking up of the lines into the s-components, the p-components being invisible.

It is to be mentioned here that in this work the inverse Stark effect, i.e., the effect of an electric field on the absorption spectrum, is to be used. No work on this subject is to be found in the literature, but it stands to reason that if a magnetic field has the same effect on the absorption as on the emission spectrum an electric field ought to do likewise.

1. J. Stark- Annalen der Physik.



1. The first part of the paper is devoted to a general discussion of the problem of the existence of a solution of the system of equations (1) in the case of a linear operator. It is shown that the existence of a solution is equivalent to the solvability of a certain boundary value problem for the Laplace equation in the upper half-plane. The problem is solved by the method of conformal mapping. The solution is expressed in terms of the boundary values of the function. The existence of a solution is proved for a certain class of boundary values. The solution is unique. The problem is solved for a certain class of boundary values. The solution is unique. The problem is solved for a certain class of boundary values. The solution is unique.

2. The second part of the paper is devoted to a general discussion of the problem of the existence of a solution of the system of equations (1) in the case of a nonlinear operator. It is shown that the existence of a solution is equivalent to the solvability of a certain boundary value problem for the Laplace equation in the upper half-plane. The problem is solved by the method of conformal mapping. The solution is expressed in terms of the boundary values of the function. The existence of a solution is proved for a certain class of boundary values. The solution is unique. The problem is solved for a certain class of boundary values. The solution is unique.

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## II. Concerning Photochemical Reactions in General.

In the literature which has to do with Photochemistry there appear many contradictions. These, no doubt, arise from the difficulty of experimentation in the subject and the many small things which have to be taken into account. The authority on the subject of Photochemistry is J. Plotnikow, but even in his work many contradictory statements are found. We, then, beg to be excused for any mistakes we may make in setting forth the general principles of Photochemistry.

Reactions which are either initiated or accelerated by radiant energy, the wave-length of which corresponds either to the visible spectrum or to the ultra-violet, are termed photochemical reactions.<sup>1</sup> The photoactive rays stretch from  $\lambda 8000$  A. U. down to about  $\lambda 3000$ . Probably the first observed photochemical reaction was the development of green color in plants due to the light of the sun and their bleaching in the dark. Other well-known reactions of this type are: The combustion of hydrogen and chlorine, the polymerization of anthracene, ~~and~~ the reduction of silver salts on which photography is based, the depolymerization of ozone, the oxidation of lead sulphide.

Two fundamental generalizations were enunciated by Grotthuss in 1818. However, only the first is found to be valid up to the present day. Grotthuss' first law is this ~~this~~: ONLY THOSE WAVES WHICH ARE ABSORBED BY THE SUBSTANCE CAN BE CHEMICALLY ACTIVE. The converse of this proposition is not necessarily true as there are a number of substances which take up light of a certain frequency and are not activated by that light. Plotnikow makes a few generalizations about photoactivity which follow:

1. Each element which possesses free valence electrons is photochemically

1. J. Plotnikow- Lehrbuch der Photochemie.

2. W. C. McC. Lewis- A System of Physical Chemistry Vol II.



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active.

2. The photoactivity of the elements is a function of their periodicity.
3. Light has the power to turn a photochemically unsaturated system into a saturated one, whether during the process work is done on or by the system.
4. Each photochemically unsaturated union is photoactive.

Let us consider now the kinetics of photochemical reactions. It has been found that, OTHER THINGS REMAINING THE SAME, THE REACTION VELOCITY IS DIRECTLY PROPORTIONAL TO THE LIGHT INTENSITY. Here we must divide photochemical reactions into two classes: 1. Reactions which are originated by light, i.e., they will not go in the dark; and, 2. reactions which go very slowly in the dark but are catalysed by light. The reactions which belong to these two classes will be discussed in a later paragraph.

According to the Law of Mass Action, the rate of the dark reaction is given by the expression-

$$V_1 = k[A]^a[B]^b$$

where a and b are the concentrations of A and B respectively. If the same reaction takes place in the light we have the following expression for the velocity-

$$V_2 = k[A]^c[B]^d$$

where c and d are new constants determining the order of the reaction in the light. In general a and b are not the same as c and d. Usually c and d are less than a and b. The total velocity, then, of a reaction in the light is

$$V = k_1[A]^c[B]^d + k_2[A]^a[B]^b$$

and if the intensity of the light is I, then

$$V = k_1[A]^c[B]^d + k_2[A]^a[B]^b I$$







It is seen that if  $k_1=0$ , we have a pure "Lichtreaktion", i.e., a reaction which belongs to the first class; and if  $k_2=0$ , then we have a pure dark reaction or one which is not catalysed by light.

Equilibrium in the photochemical sense differs from our usual conception. In the case of ordinary catalysis we know that the catalyst does not shift the position of equilibrium. However, in the case of photochemical catalysis the equilibrium with the <sup>light</sup> on is different from that in the dark. In the case of reversible photochemical reactions the "equilibrium" or "photo-stationary" state is obtained only so long as the light is on; and when the light is turned off the reaction reverts to its dark equilibrium point. This is known as the PRINCIPLE OF STATIONARITY. A notable instance of this is found in the transformation of dianthracene into anthracene.

Another phenomenon of photochemical reactions is the so-called induction period. This is the initial period in which no reaction appears to take place, or in which the reaction <sup>goes</sup> very slowly, but after which the reaction attains its normal velocity. This effect was observed by Bunsen and Roscoe and also Plotnikow in the combustion of hydrogen and chlorine, but some doubt has since been entertained as to its true existence.

Photochemical reactions may be divided into two main groups. According to the principles of thermodynamics a reaction, when uninfluenced by outside agencies, takes place with a decrease of free energy. When light falls on a system <sup>it</sup> it may act in either of two ways: The reaction may go the natural way i.e., with a decrease of free energy, or it may oppose the chemical forces and proceed with a gain of free energy. In the second case it will be noted that as soon as the light is shut off the reaction reverses and goes with a decrease in free energy. Here a stationary state is reached. We shall now classify photochemical reactions in the following

1. J. Plotnikow- Lehrbuch der Photochemie.
2. W. C. McC. Lewis A System of Physical Chemistry, Vol II.



It is seen that in this case the light is not reflected at the surface of the medium, but is refracted into it. This is the case when the angle of incidence is less than the critical angle. When the angle of incidence is greater than the critical angle, the light is totally internally reflected. This is the case when the angle of incidence is greater than the critical angle. The critical angle is the angle of incidence for which the refracted ray travels along the boundary between the two media. For angles greater than this, the ray is reflected back into the denser medium. This is the principle of total internal reflection, which is the basis of optical fibers and many other optical devices. The critical angle depends on the refractive indices of the two media. It is given by the equation  $\sin \theta_c = \frac{n_2}{n_1}$ , where  $n_1$  is the refractive index of the denser medium and  $n_2$  is the refractive index of the less dense medium. This equation shows that the critical angle is smaller for a larger difference in refractive indices. For example, the critical angle for light traveling from water to air is approximately 48.6 degrees, while for light traveling from glass to air it is approximately 41.5 degrees. Total internal reflection is a key concept in understanding the behavior of light in various optical systems, including lenses, prisms, and fiber optic cables.



manner:-

I. Reactions involving an increase in free energy.

Here we have such reactions as the decomposition of dianthracene into anthracene, and the oxidation of hydrogen iodide to iodine.

II. Reactions involving a decrease in free energy.

a) Pure photochemical reactions. To this class belong the oxidation and reduction of several organic compounds, and the reduction of silver bromide and chloride as on the photographic plate.

b) Photo-catalytic reactions. The most important reactions belonging to this class are- The oxidation of oxalic acid into carbon dioxide and water, the combination of carbon monoxide and chlorine to form phosgene and the photochemical combustion of hydrogen and chlorine. These reactions all take place to a certain extent in the dark but are catalysed very highly by light. Of the three the reaction of hydrogen and chlorine has been most thoroughly studied.

Before going on with the history of experimentation on the hydrogen-chlorine reaction, let us mention one more law has an important bearing on photochemistry in general. This is Einstein's Law of the Photochemical Equivalent, and is the result of the application of the quantum theory to photochemical reactions. It states that EACH SINGLE MOLECULE OF A PHOTO-SENSITIVE SUBSTANCE REQUIRES JUST ONE QUANTUM  $h\nu$ , (of the requisite frequency  $\nu$ , which the substance can absorb) IN ORDER THAT IT MAY REACT. This law has been tested out and has been found to hold approximately, the exceptions being where some integral multiple of a quantum is required instead of one quantum.

There has been a good deal of work done on the photochemical reaction of hydrogen and chlorine extending over a long period of years. The reaction

1. W. G. McC. Lewis- A System of Physical Chemistry, Vol III







was first thoroughly examined by Bunsen and Roscoe. It had been the subject of an earlier work by Grotthuss and Draper from which the Grotthuss Absorption Law was enunciated.

Bunsen and Roscoe measured the hydrochloric <sup>acid</sup> formed by means of an accurate actinometer. They found that the reaction takes place more readily when the reacting gases are moist than when they are dry. They also studied the so-called induction period and found that the sensitivity of the reactants increased over a period of six days, reaching a maximum at the end of that time. They also found that oxygen decreased the length of the induction period. Others, including Plotnikow, studied the reaction and found that it went slowly in the dark and that the blue and violet rays which activated it were only slightly absorbed by it- a thing which which seems absurd if we consider the work of Mrs. Laird on the absorption spectrum of chlorine.

Recently an interesting piece of work by Trautmann has appeared which throws light on the subject. He used a method of sealing measured portions of hydrogen and chlorine up in tubes, letting them react under the influence of light and then titrating the hydrochloric <sup>acid</sup> formed with base and the chlorine left by adding potassium iodide and titrating with thio-sulphate solution. He found that practically the reaction took place when the gases were dry. It also appeared that oxygen acted as an inhibitor, small quantities cutting down the reaction very greatly.

### III. Experimental

The problem that we undertook is along the same line as Grotthuss' Law. It will be recalled that Grotthuss' Law states that only those waves which are absorbed by a substance can activate it photochemically. Our problem is to show that IT IS THOSE DEFINITE FREQUENCIES WHICH ARE SHOWN IN THE LINE SPECTRUM OF CHLORINE WHICH ACTIVATE THE PHOTOCHEMICAL COMBUSTION

1. H. Trautmann- Zeitschrift für Physikalische Chemie, 105 Band, 5/6 Heft.



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OF HYDROGEN AND CHLORINE. By this we mean that it is not just the general absorption in the green and the blue stretching from  $\lambda 4799$  to  $\lambda 5350$ , but the definite frequencies, lines, themselves which activate the reaction.

If the reaction is activated by light absorbed by either one of the reactants it must be by that absorbed by the chlorine, since hydrogen does not absorb in the visible spectrum. It has been shown that when a layer of chlorine is interposed between the source of light and the reaction vessel that the reaction is cut down. This shows that it is the light absorbed in the range from  $\lambda 4799$  to  $\lambda 5350$  which activates the reaction. It does not show, however, that it is the definite lines of the chlorine spectrum which activate it.

To show that it is the definite frequencies of the line spectrum of chlorine which activate the reaction one must go about it in the following manner. By interposing a layer of chlorine between the source of light and the reacting gases we are able to show that the reaction is screened, either 1) due to the cutting out of the definite lines of the chlorine spectrum, or 2) by general absorption in the blue and green. If the former case is true we could show it by breaking up the lines into components in some manner. When this is done we no longer have the original lines of the chlorine spectrum present while we do have the same general absorption in the green and the blue. If the amount of hydrochloric acid formed when the spectral lines of chlorine are shielded from the reactants by an absorption tube is less than that formed when the absorption lines of the spectrum are broken up into components, it would show that the lines of the chlorine spectrum activated the reaction. If, on the other hand, no change was noted in the amount of hydrochloric acid formed when the absorption lines were present and when they were broken up, it would point to the fact that it is general absorption in the green and blue which activates the reaction.

As has already been mentioned the lines of an absorption spectrum



The first part of the paper is devoted to a general discussion of the problem of the existence of a solution of the system of equations (1) in the case of a linear operator. It is shown that the existence of a solution is guaranteed if the operator is linear and the right-hand side of the system is a linear function of the variables. The second part of the paper is devoted to a study of the problem of the existence of a solution of the system of equations (1) in the case of a nonlinear operator. It is shown that the existence of a solution is guaranteed if the operator is nonlinear and the right-hand side of the system is a nonlinear function of the variables. The third part of the paper is devoted to a study of the problem of the existence of a solution of the system of equations (1) in the case of a linear operator with a delay. It is shown that the existence of a solution is guaranteed if the operator is linear and the right-hand side of the system is a linear function of the variables. The fourth part of the paper is devoted to a study of the problem of the existence of a solution of the system of equations (1) in the case of a nonlinear operator with a delay. It is shown that the existence of a solution is guaranteed if the operator is nonlinear and the right-hand side of the system is a nonlinear function of the variables.



may be broken up into three components by making use of the Zeeman effect. It will be remembered, however, that a field of from 20,000 to 50,000 C. G. S. units must be applied. As a layer of from twelve to fourteen inches of chlorine is necessary to screen the reaction appreciably the experimental difficulties of placing such a field on the absorbing layer would be very great. If, however, we make use of the inverse Stark effect for spreading the lines we will meet with fewer difficulties. In this experiment we will make use of an electrostatic field for breaking the absorption lines of chlorine.

#### Apparatus-

The method used in this investigation is of the dynamical or flow type. It consists of letting an approximately equivalent mixture of hydrogen and chlorine flow through a reaction tube which is placed in front of a source of light. At first hydrogen was obtained from a tank, scrubbed with water and dried by passing through concentrated sulfuric acid. Chlorine was also obtained from a tank and purified in the same manner. Certain changes have now been made in the method of preparation of hydrogen and chlorine which will be discussed in a later paragraph. The line containing the mixed chlorine and hydrogen is protected from the light by a coating of black paint except for a small place about three inches long where the light from a projection lantern is admitted. In this space the reaction occurs. The gases, consisting of hydrogen-chloride, chlorine and hydrogen, are then led into a water absorber where the hydrochloric acid is absorbed; they are then discharged into concentrated alkali to absorb the waste chlorine. The source of light, situated about a foot and a half from the reaction tube, is a projection lantern of medium size. The amount of hydrochloric acid formed is determined by titration with NaOH.

A series of runs was taken using this apparatus to see if the intensity







of the light were strong enough and if the apparatus would work. Approximately equal parts of chlorine and hydrogen were obtained by counting the number of bubbles of each that passed in a given time. A fifteen minute run was taken in the dark, and another with the projection lantern on. On titrating it was found that the chlorine absorbed by the water bleached the indicator (methyl red). This was obviated by boiling the solution before titration. The results which were obtained agreed very well among themselves. They run as follows:

(The figures given are in ccs. of <sup>0.01</sup>~~0.001~~ N NaOH taken to neutralize the HCl formed)

Dark	Light
3.2	49.9
17.2	63.3
6.5	<del>64.1</del> 38.4
3.0	64.1

From these results it is seen that the reaction goes slowly in the dark as is shown by the small amounts of hydrochloric acid formed. Part of this formed in the dark may be due to hydrolysis of the chlorine. It is also to be noted that no long induction effect is found here.

The next step was to find what thickness of chlorine was necessary to give a measurable screening effect. To this end a two liter flask filled with chlorine was placed between the light and the reaction tube, and runs taken with it. To give a check on the amount of acid formed in the dark a fifteen minute run was taken in the dark. To eliminate the effect of the scattering of the light by the flask a run was taken with the empty flask interposed between the source of light and the tube. On this set of three runs the following data were obtained:

Dark	With empty flask	With flask of Cl
4.3	28.5	24.0
3.0	30.9	27.0



of the light rays passing through the lens, and it is the spectrum of the light rays which is observed. The number of rays of light which pass through the lens is proportional to the area of the lens, and the number of rays which pass through the lens is proportional to the area of the lens. The number of rays which pass through the lens is proportional to the area of the lens. The number of rays which pass through the lens is proportional to the area of the lens.

Results are as follows:

(The figures given are in units of 10<sup>10</sup> photons per second per square centimeter.)

(1) Results

Wavelength (Å)	Intensity (photons/cm <sup>2</sup> /s)
4000	1.0
4500	1.5
5000	2.0
5500	2.5
6000	3.0
6500	3.5
7000	4.0
7500	4.5
8000	5.0
8500	5.5
9000	6.0
9500	6.5
10000	7.0

From these results it is seen that the number of photons per second per square centimeter is proportional to the wavelength of the light. This is in agreement with the results of the experiment. The number of photons per second per square centimeter is proportional to the wavelength of the light. This is in agreement with the results of the experiment.

It is also to be noted that the number of photons per second per square centimeter is proportional to the wavelength of the light. This is in agreement with the results of the experiment. The number of photons per second per square centimeter is proportional to the wavelength of the light. This is in agreement with the results of the experiment.

The next step was to find what thickness of material was necessary to give a measurable amount of light. It was found that a thickness of 1 cm of material was necessary to give a measurable amount of light. This is in agreement with the results of the experiment.

Wavelength (Å)	Intensity (photons/cm <sup>2</sup> /s)	Thickness (cm)
4000	1.0	1.0
4500	1.5	1.0
5000	2.0	1.0
5500	2.5	1.0
6000	3.0	1.0
6500	3.5	1.0
7000	4.0	1.0
7500	4.5	1.0
8000	5.0	1.0
8500	5.5	1.0
9000	6.0	1.0
9500	6.5	1.0
10000	7.0	1.0

From these results it is seen that the number of photons per second per square centimeter is proportional to the wavelength of the light. This is in agreement with the results of the experiment. The number of photons per second per square centimeter is proportional to the wavelength of the light. This is in agreement with the results of the experiment.



A six liter flask of about one foot diameter was next tried in the same manner. Unfortunately part of the apparatus broke after one run so that a check could not be obtained. The amount of absorption is given as follows:

Dark	Empty flask	Filled with Cl
8.3	121.5	33.2

With the aid of this data an absorption tube was made to which an electrostatic field could be conveniently applied. The tube is 14 inches in length and 2 1/4 inches in diameter. It is made of glass with parallel plates of glass cemented on each end with a cement made by mixing water glass and asbestos. The joint is then made chlorine-tight by painting over with paraffin. Stop-cocks are placed in the side of the tube so that it may be filled with chlorine at will.

At first it was thought that an electrostatic field could be applied externally to the tube. Two blocks of wood covered with sheet lead were placed on either side of the tube. These were charged by a small Helmholtz machine, which was driven by a motor. A field, estimated by spark discharge to be about 20,000 volts, was maintained across the plates. Duplicate runs were taken in the following manner. The tube was filled with chlorine, from a tank and purified as before mentioned; a run was taken with the field on, with no field on, in the dark, and in the light with no chlorine in the tube, and the following results obtained:

	Acid Formed	
Dark	3.4	5.0
Light (no chlorine in the tube)	59.6	91.2
Absorption (chlorine in the tube)	10.6	10.3
Field (field on)	10.2	10.5

It will be seen that no change is observed when the field is put on. This is probably due to the fact that the field on the chlorine in the tube



A list of about 100 names was sent to the  
 various departments of the Government and  
 that a check might be obtained. The names of  
 the following:

1917	1918	1919
1920	1921	1922

It was found that in 1917 and 1918  
 the names of the following were  
 listed as being in the service of  
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 following were listed as being in  
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 the Government in 1917 and 1918.  
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 listed as being in the service of  
 the Government in 1919 and 1920.  
 The names of the following were  
 listed as being in the service of  
 the Government in 1921 and 1922.

1917	1918	1919
1920	1921	1922

It will be seen that the names of the  
 following were listed as being in  
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 the service of the Government in  
 1919 and 1920. The names of the  
 following were listed as being in  
 the service of the Government in  
 1921 and 1922.



is too small to produce a Stark effect, since the lines of force would have a tendency to follow the outlines of the glass tube rather than go through it.

In order to get a sufficient field plates were put inside the tube in the following manner. Strips of glass 12" by 1" by 1/8" were cut and ground on both sides. These were coated with graphite and supported in the tube by means of mica supports. Mica discs were cut, having an opening in the center to permit the passage of light and keeping the plates parallel to each other at a distance of one inch. Connection was made to the outside with platinum foil. The foil was cemented onto the plate with some of the silica cement, and was led outside through the cement of the glass plates on the ends of the tube. A band of shellac was painted about one inch from each end on the outside of the tube to stop any electrical leak that might be caused by the conductivity of the cement. The tube was connected up to the Helmholtz machine and runs taken as before.

At this stage an electrolytic hydrogen and chlorine generator was installed to take the place of the tanks. The generator consisted of a bottle containing concentrated hydrochloric acid and salt into which dipped two platinum electrodes. A current of 2 amperes was run through it giving gases at about the same rate as did the tanks. The issuing gases were washed with and dried with concentrated sulfuric acid. Chlorine for the absorption tube was generated by letting concentrated hydrochloric acid react with  $KMnO_4$ . Several runs were taken with the following results:

Dark	Light	Absorption	Field
12.2	208.4	6.9	16.4
5.1	356.3	10.5	20.8
7.4	20.3	11.4	23.5
-----	-----	8.4	30.0

The amount of acid formed when the field is on in every case is greater than



In the first instance, the author has endeavored to present a clear and concise account of the various methods of determining the relative humidity of the air, and of the various factors which influence its amount. The author has also endeavored to present a clear and concise account of the various methods of determining the relative humidity of the air, and of the various factors which influence its amount.

Temperature	Relative Humidity	Wet Bulb Temperature	Dew Point
70	50	55	45
75	50	60	50
80	50	65	55
85	50	70	60
90	50	75	65
95	50	80	70

The amount of water vapor in the air is an important factor in determining the relative humidity of the air, and is an important factor in determining the amount of water vapor in the air.



that formed when no field is on, but the difference between the two is so small and the precision of measurement is so poor that it is hard to say whether the increase in acid formed is the result of the field or is pure chance. It was found, that due to an electrostatic leak where the platinum foil was attached to the plates, that there was only a small field in the tube.

The leak was remedied by sealing platinum contacts through tubes in the side of the absorption tube. Platinum wires were sealed into small glass tubing and these in turn were sealed into the opposite sides of the absorption tube at an angle of 45 degrees from the vertical. Contact was made through mercury to wires leading to an induction coil. The platinum wires made contact with the back of the glass plates. An induction coil was used instead of the Helmholtz machine because it gave a greater field. Five minute runs were taken instead of fifteen minute ones; they were taken in the following order: Field, absorption, dark, and light.

Dark	Light	Absorption	Field
11.7	11.5	25.9	98.5
7.6	97.8	10.4	14.0

The field held up very well during the first five minute run; it was estimated at about 50,000 volts. Toward the end of the first run, however, the graphite around the platinum contacts began to burn off due to sparking, thus accounting for the small amount of acid formed in the second run.

Graphite plates of the same dimensions as the glass ones were now obtained, and it was hoped that this would obviate any bad contact due to the wearing off of the graphite coating on the glass plates. These were placed inside the tube and the field was found to hold up perfectly, giving a spark of about one inch (50,000 volts).

In the mean time, however, it was found that no marked reaction occurred when the usual five minute run was taken in the light. Many variations of



The first part of the report is devoted to a description of the general conditions of the country, and to a statement of the results of the various expeditions which have been made since the discovery of the gold fields. It is then shown that the gold fields are situated in the western part of the country, and that they are situated in the western part of the country, and that they are situated in the western part of the country.

Year	Population	Gold	Value
1850	1000	1000	1000
1851	1000	1000	1000
1852	1000	1000	1000

The second part of the report is devoted to a description of the various expeditions which have been made since the discovery of the gold fields. It is then shown that the gold fields are situated in the western part of the country, and that they are situated in the western part of the country, and that they are situated in the western part of the country.



the experiment were tried in an attempt to secure positive results- longer runs were taken, a more intense light was used, a mirror was placed behind the reaction tube so that it received almost double the light that it had before. Intermittent runs were taken in which the gases were kept stationary in the tube for one minute while the light played on them, and were then allowed to flow for a minute and the procedure repeated until the light had been on the stationary gases for five minutes. This gave a somewhat greater amount of acid (about 20-40 cc.). However, as this was rather uncertain and as the amount of acid formed in the light was not very much larger than that formed in the dark no definite conclusions could be arrived at by any runs taken.

The following are the results of several runs using the carbon plates and taking intermittent exposure to the light as described above. The spark coil was used to give the field.

Dark	Light	Absorption	Field
5.9	16.2	5.4	5.5
8.1	40.4	6.4	6.4
12.4	21.5	13.9	8.9
----	----	11.2	10.1

It will be seen here that only a small amount of acid is formed in the light and that the value for Absorption and Field are about the same.

Another set of runs was taken, each of fifteen minutes, sweeping out with the hydrogen and chlorine mixture for five minutes before and after each run.

Dark	Light	Absorption	Field
8.7	9.6	9.0	9.7
8.0	25.1	14.6	11.7

Here we see that even less acid is formed in the light than when intermittent exposures were made. No conclusions can be drawn as to the effect of the field.







#### IV. Discussion of Results.

In our experiments we have verified the fact that a layer of chlorine when placed between the source of light and the reaction tube will screen the reaction, thus showing that the reaction is activated by light in the region of the blue and the green. A length of fourteen inches of chlorine will cut the reaction down anywhere from seventy-five to ninety per cent.

As to the fact that the definite frequencies of the chlorine spectrum activate the hydrogen-chlorine reaction, we can say nothing. We can say, however, that no appreciable field is placed on the absorbing layer unless the plates are placed inside the absorption tube. The results, in which a greater amount of acid seemed to be formed when the field was on could not be verified in later experiments using a much stronger field. Our later results were hampered by the fact that we could not get large amounts of acid formed in the light, the reason for this being unknown. Hence, we are forced to conclude that the experiments so far performed give us no clue as to the effect of the definite frequencies of the chlorine spectrum on the hydrogen-chlorine reaction.

#### V. Conclusion.

1. The photochemical combustion of hydrogen and chlorine, when screened by a layer of chlorine fourteen inches long is cut down from seventy-five to ninety per cent.

2. Whereas we have some indication that the definite frequencies of the spectrum of chlorine activate the hydrogen-chlorine reaction, due to some fault in the apparatus, no conclusive results were obtained.







VI. Acknowledgements.

I wish to express my thanks to Dr. Graham Edgar, who started this investigation, for his many helpful suggestions during the progress of the work; and also to Dr. C. M. Sparrow for his assistance on the physical side of the problem.

I wish to acknowledge my indebtedness to the American Association for the Advancement of Science for a grant made to Professor Graham Edgar, which aided materially in defraying the expenses of this investigation.

University, Va.

May 15, 1924.

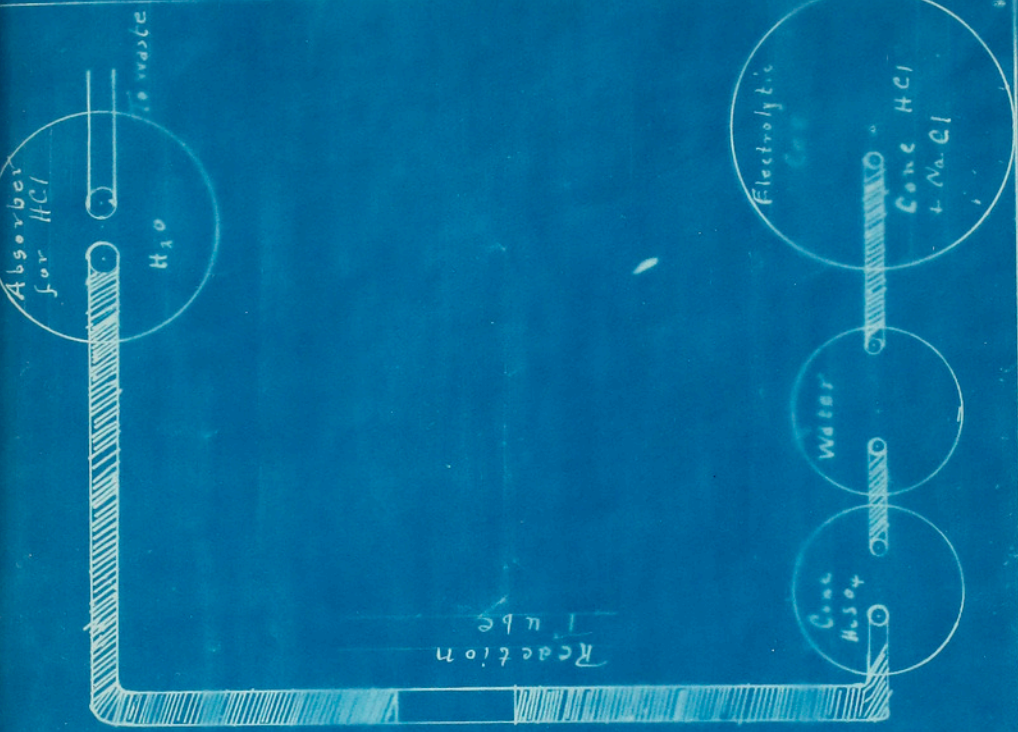
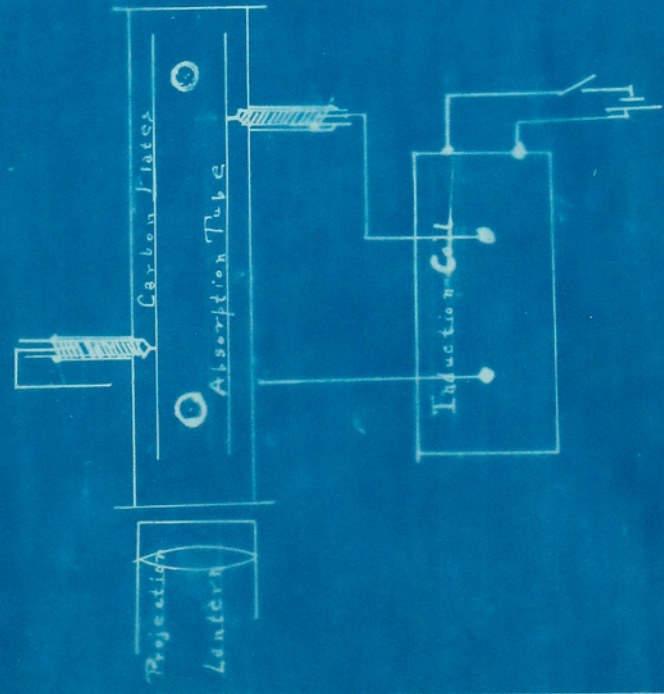
Allan C. G. Mitchell





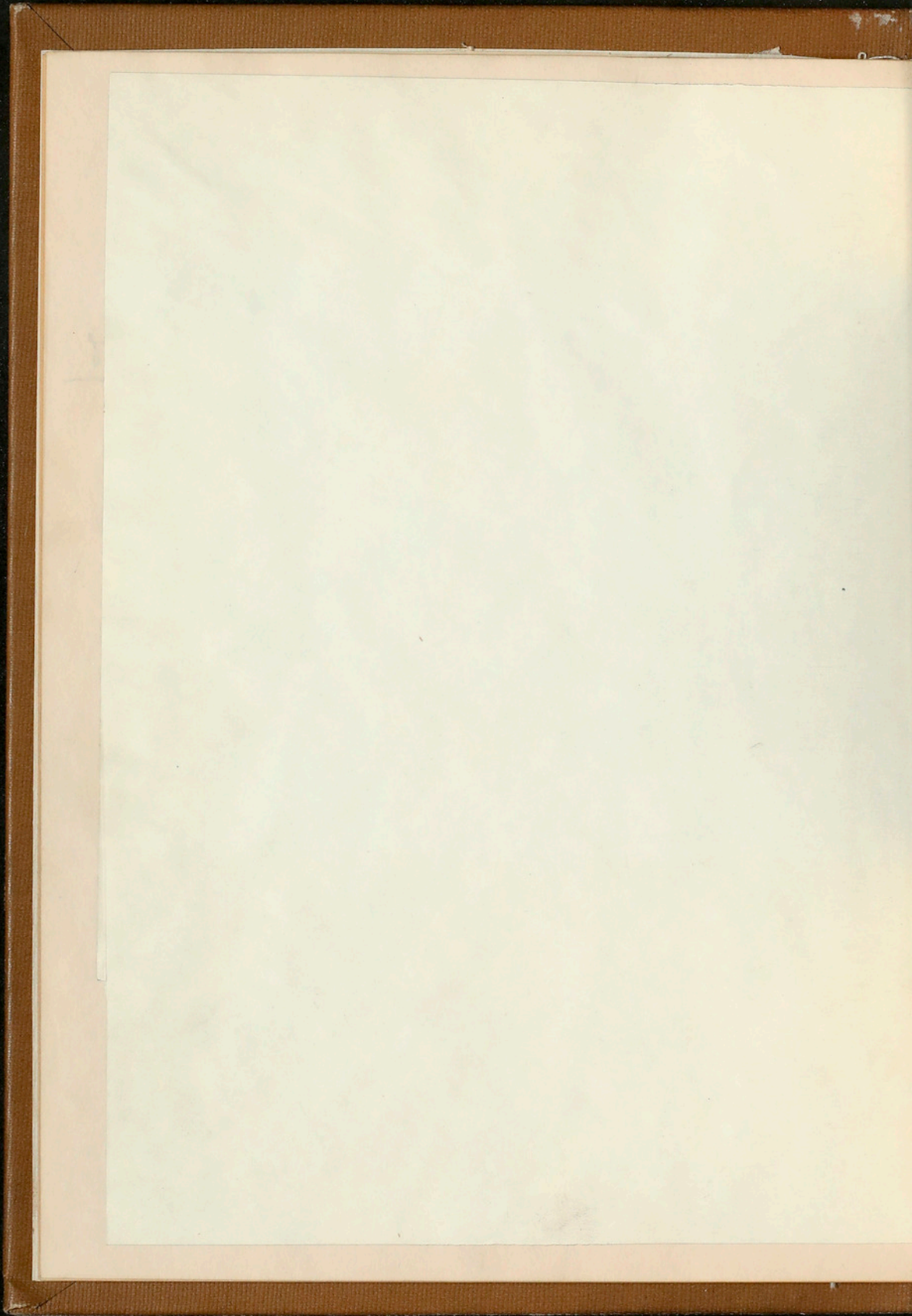


Plate I



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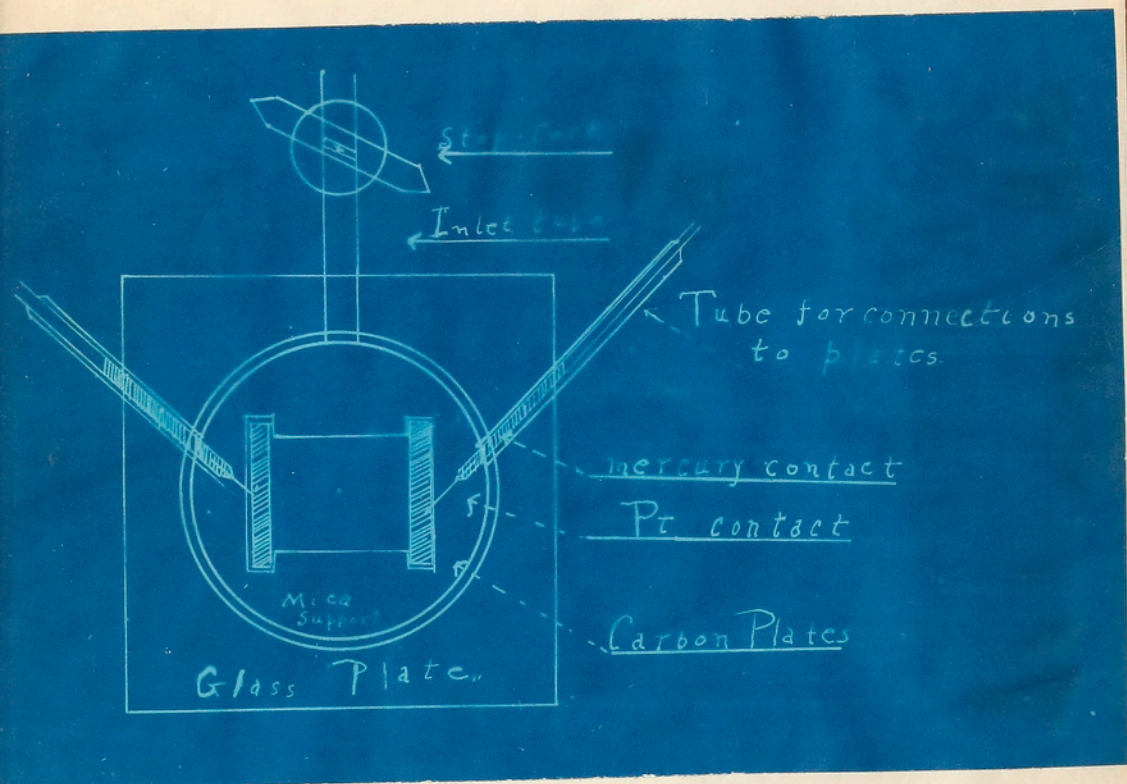
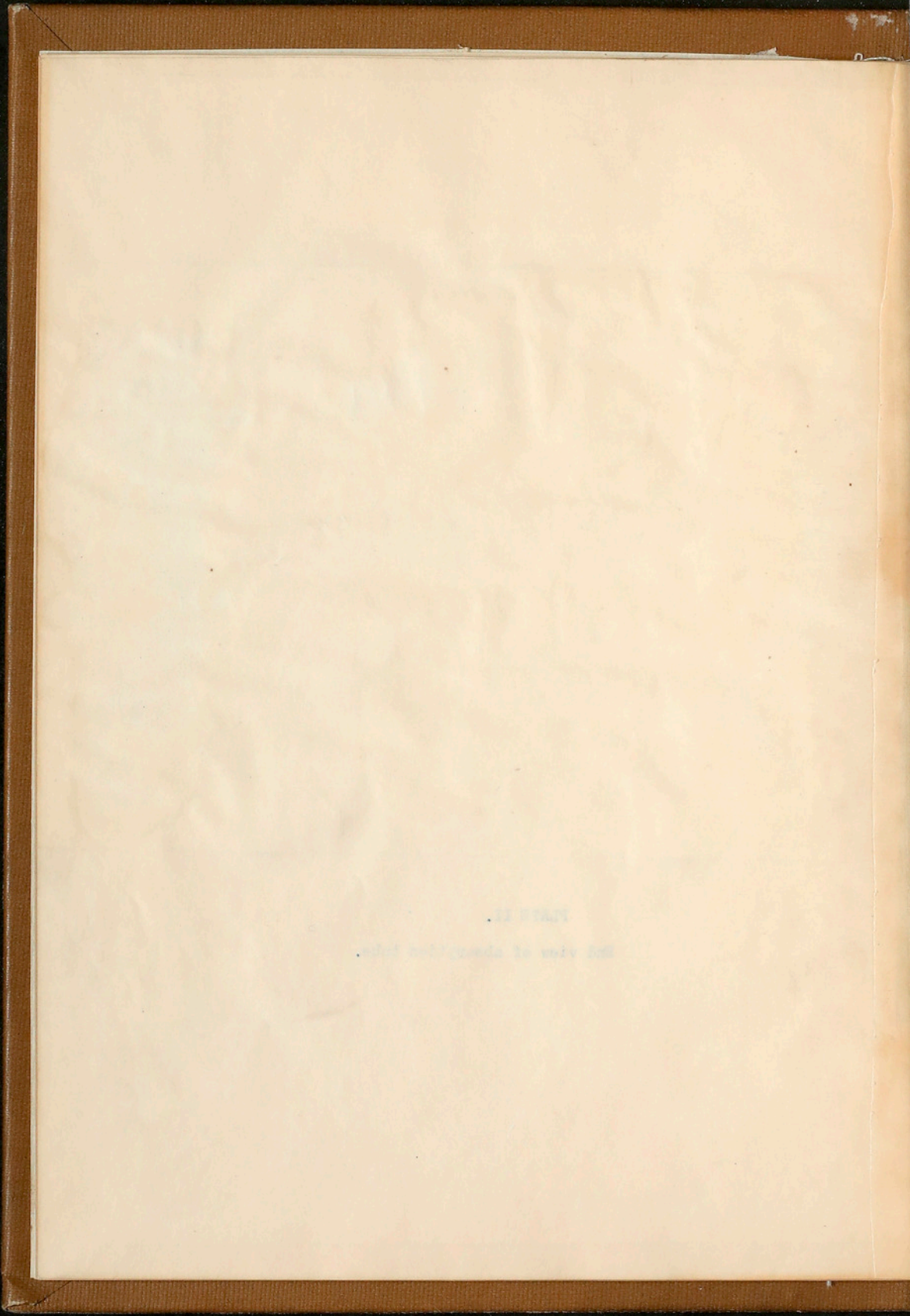


PLATE II.

End view of absorption tube.

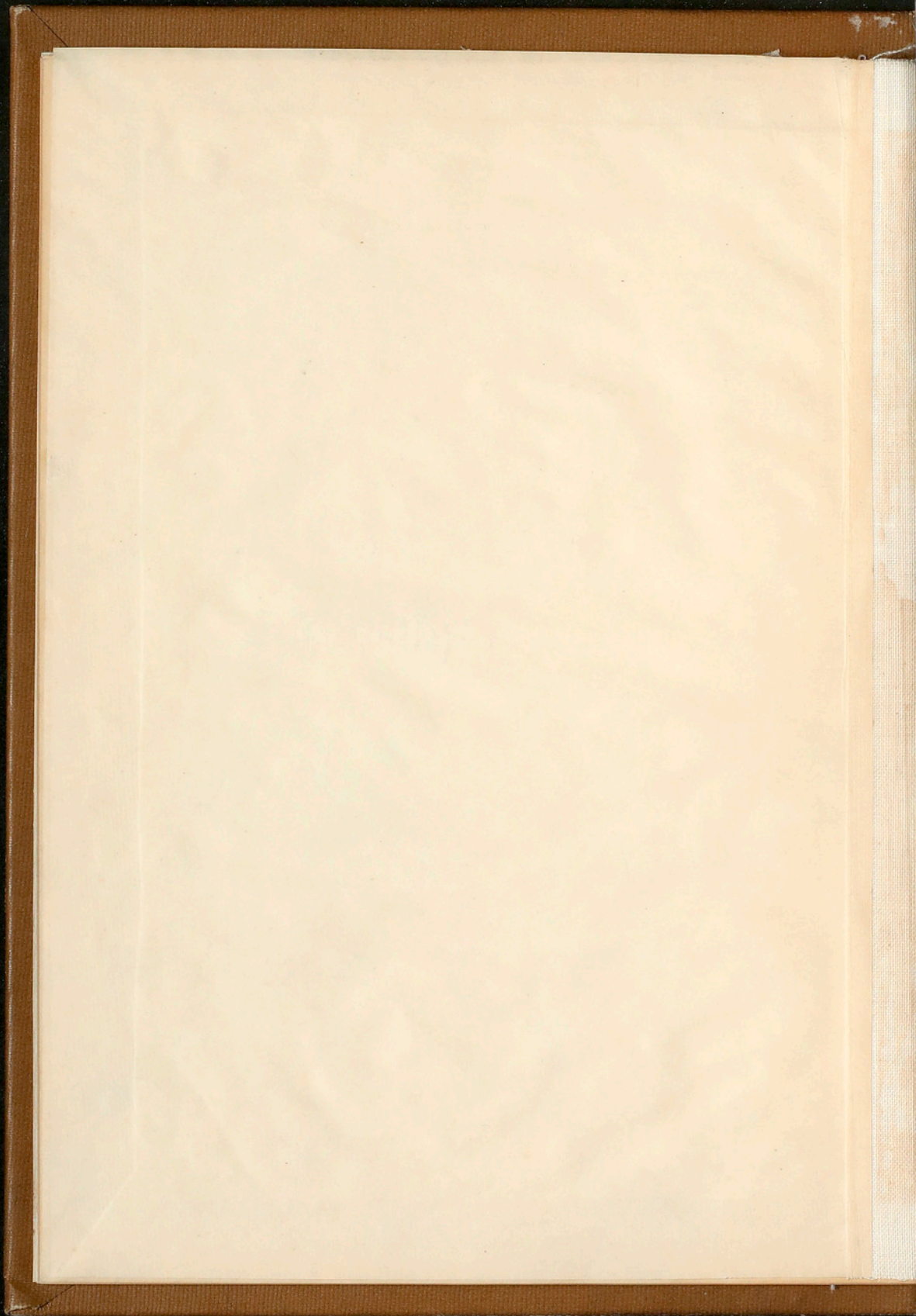














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