# STUDIES
# IN
# PHOTOCHEMISTRY

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A Dissertation by

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## To the examiners.

In order to assist in the examination of this dissertation the following outline pointing out the original work carried out by the author, has been compiled.

To begin with this photochemical study was the first study of its kind to be undertaken in the Department at McGill and hence the whole of the technique was new to the author. For this reason it had to be worked out without the assistance or experience which would have been gained had any work of such a nature been carried out previously in the Department.

A number of improvements have been added to the technique of photochemistry. These have been stated on page 153, the details of which are given in the earlier sections. To these might be added some others as follows;

1. The use of a reaction cell with a section at the end which could be evacuated and kept warm so that no condensation of moisture on the window could take place;

2. the employment of printing out paper for determining the area of the light beam.

3. the use of a tube filled with solution of a red dye to act both as a lens and as a protection from light , for the capillary indicating tube.

4. the following of the reaction by the change in light absorption.

In connection with these methods (1-4) the author knows of know work in which the above have been used ,although a complete literature search has not been made ( $>$ 250 papers ).

The new work from the theoretical standpoint has been summarized on page 155. and requires no further comment here.

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# SECTION I

# INTRODUCTION

## 1. The Problem and Method of Attack.

A study of certain aspects of the photosynthesis of hydrogen chloride has been made. In this study particular attention has been given to the following points: the temperature coefficients of the light absorption and of the quantum yield, for different wave-lengths; the so-called photochemical threshold; the variation of quantum yield with light intensity; and the effect of the walls on the chain character of the reaction.

Two general methods were employed in attacking the problem. The first was a modified Bunsen-Roscoe Technique. Filtered monochromatic light from a mercury arc was passed into a reaction cell containing besides hydrogen and chlorine at atmospheric pressure a small volume of water to absorb the hyrdogen chloride formed. The rate of reaction for different temperatures was followed by the movement of a water index in a horizontal capillary tube connected with the cell and open to the atmosphere. Instead of the usual practice of employing electrolysed hydrochloric acid as the source of hydrogen and chlorine, cylinder gases were used, the hydrogen being fractionally distilled in vacuo using liquid air. The intensity of the light was measured by means of a thermopile.

In the second method a modified Bodenstein Technique was used. Spectrally dispersed light, from two monochromators in series, was passed through a reaction cell containing hydrogen and chlorine and into a thermopile. The extent of the reaction was followed by freezing out the chlorine and hydrogen with liquid air, pumping off the hydrogen and determining the pressure of the remaining chlorine at room temperature using a glass diaphragm manometer. The number of quanta of a given wave-length absorbed was determined using a thermopile.

The method used in presenting this dissertation is as follows: a general introduction is given showing the importance of photochemistry and its related fields, followed by an introduction to the photosynthesis of hydrogen chloride. (For the sake of brevity this reaction is referred to throughout as the hydrogen-chlorine reaction. When the thermal union is meant the term thermal reaction is stated.) Following a brief historical account of photochemistry and the hydrogen-chlorine reaction, the experimental is given in three parts: the purification of materials; experiments using the Modified Bunsen-Roscoe Technique; experiments using the Modified Bodenstein Technique. The results of the two methods and a working hypothesis is discussed based on the experimental evidence to date. The conclusion and summary follow.

## 2. Introduction to Photochemistry

It is only in the present century that photochemistry or the study of chemical changes induced by radiation has developed its individuality and it must now be considered as one of the most valuable instruments for the elucidation of the true mechanisms of chemical processes and the study of free radicals.

The slow development of photochemistry compared with other branches of physical chemistry is possibly due to two main causes. On the one hand, the experimental study of photo-processes involves in general a somewhat difficult technique in order to obtain data of real value; on the other hand, the development of the theoretical side had to await the coming of the quantum theory.

It was natural that the function of light energy absorbed by a photochemical system was considered to supply the energy of activation, but the absence of any idea as to the manner in which the activation was brought about or the amount of energy thereby supplied to the individual molecule prevented any real advance. Investigators usually confined themselves to fitting their experimental results to a modified mass law expression such as: rate of reaction = $k I (A)^a (B)^b$

The advent of the quantum theory partially supplied the answer to these problems and completely revolutionized the study of photochemical kinetics. The application of this theory by Einstein together with the work in modern physics, on the origin of line and band spectra, has supplied the necessary background for the evolution of photochemistry and has stimulated a new interest in the subject.

A complete study of a photochemical reaction requires, in the first place, a knowledge of the line and band spectra concerned; in the second place, the measurement of the number of quanta absorbed; and in the third place a kinetic study of the process. The first two studies usually furnish the clues necessary for a successful handling of the kinetics. Herein lies the importance of photochemistry as a means for the elucidation of the mechanism of chemical reactions, since a great many thermal and photochemical reactions have identical mechanisms.[1-4] Furthermore the first information that has ever been obtained about the kinetics of reactions between free atoms was determined in this manner by

Bodenstein [5,6] for bromine. Often the photochemical and thermal mechanisms are quite different.[7,9,10,11] At the same time there are a number of photo-chemical reactions which have not been realized thermally.[8]

The conception of chain reactions originally proposed by Bodenstein [13] to explain the larger photochemical yield in the hydrogen chloride reaction has been extended to thermal reactions. The prominent part played by chain reaction mechanisms in the processes of chemical change has become very evident during the last few years [12].

Just as the quantum theory gave photochemistry a new life, so has the application of the experimental evidence and theories, obtained from modern spectroscopy, done likewise. It is only within the last five or six years that the importance of the application of this evidence and the inadequacy of any photochemical study without it, has been appreciated.

Spectroscopy admittedly is not the language of the chemist, but just as the photochemist has been rewarded by its study, so should workers in other branches of chemistry profit likewise. As the direct application of spectroscopy to photochemistry will be given in considerable detail later it will not be discussed at this point. It would take many pages to describe the application of the study of spectra to chemistry. However, it may not be out of place to devote a few pages here to illustrate its direct application to physico-chemical problems.

An answer to the difficult question of the electron grouping in the elements and the key to the understanding of the periodic system was actually reached in 1925[14] and 1926 on the basis of spectroscopic observations and the Pauli Principle.

A systematic investigation of the symmetry relationships of atoms with different numbers of electrons, in quantum mechanical resonance, in conjunction with the Pauli Principle, gives most of the known facts about chemical valency in a qualitatively correct manner[15,16,17]. It must be pointed out, however, that the Pauli Principle is purely empirical and not inherent in the quantum mechanical theories. It is probably just as empirical as the rules of valency established by chemistry alone. The significant fact from the point of view of photochemistry is the striking relation between the facts of chemistry and those of spectroscopy, crystallized in the statement that the chemical valency is one less than the spectral multiplicity.

Band spectra furnish a very accurate method of determining the heats of dissociation of molecules, for example the heats of dissociation of chlorine [18,21,22,23,24], bromine [18,21], iodine [18,19,20], oxygen [25], hydrogen [26,27], have all been obtained and agree quite well with the accepted calorimetric figures. In most cases the spectroscopic method is the more accurate.

From a knowledge of the energy levels of a molecule and their statistical weights, as determined from band spectra, it is possible to calculate not only the specific heat of the gas but also (making use of the Sackur Tetrode equation) its absolute entropy. Giauque and Wiebe [31] made such entropy calculations for hydrogen chloride, hydrogen bromide, hydrogen iodide and oxygen. They have compared the results with those obtained from direct calorimetric measurements, assuming the correctness of the third law of thermodynamics. In all cases the agreement is excellent. Giauque has also calculated free energy values from spectroscopic data [28].

Any difference in the weight of the nuclei in a molecule makes a considerable difference in the spacing of the vibrational and rotational levels. By studying this difference the existence of isotopes of oxygen, carbon and nitrogen, as follows ( $O^{16}\ O^{17}$ and $O^{16}\ O^{18}$, $C^{13}$ and $N^{15}$ ), has been proved [29,30].

The equilibrium $I_2 = 2I$ has been determined from spectroscopic data alone. More remarkable still, the energy of dissociation of the hydrogen molecule has been determined by wave mechanics alone by Sugiura [32] and Wang [33].

Since the existence of every material particle is bound up with an oscillatory process, both from the de Broglie point of view (electrons, [34,35] hydrogen and helium beams may be reflected and diffracted from crystal surfaces in a wave like manner) and the quantum resonance point of view, the understanding of this so-called quantum mechanical resonance idea is one of the most interesting problems in photochemistry to-day. Again, since according to Hinshelwood [41] the vibrational quanta are the significant ones in the process of chemical activation, the importance of the understanding of the above phenomena is obvious.

The question of what is the diameter of a normal and an excited molecule is one of the most important from the standpoint of chemical kinetics. Related to this, again, is the question of the influence of one molecule on another at distances far greater than the kinetic theory collision diameters. Experiments in which the intensity of the fluorescence of mercury [42,43] and other vapors, such as nitrogen dioxide [44] and sodium [45], in the presence of varying pressures of foreign gases has been measured, show that the power to deactivate excited molecules varies considerably with different gases, and depends not only on the nature of the gas but also on the nature of the excited atom. As a general rule oxygen is among the most efficient and the inert gases the least efficient. In the case of excited mercury atoms oxygen is roughly three thousand times as efficient as helium, For example, if every collision between excited mercury atoms and an oxygen molecule leads to deactivation of the atom,only one in every three thousand collisions between helium and mercury does so. Even if it is assumed that every collision between oxygen and excited mercury atoms leads to deactivation, the results obtained show that the collision diameter of the excited mercury atom is many times greater than the normal mercury atom, a result which must be borne in mind when reactions involving excited molecules are considered. This ineffectiveness of the inert monatomic gases with no vibrational quanta is quite significant.

Absorption spectra have been used for years to determine the presence and concentration of certain molecules. Among the recent interesting applications is the demonstration of the existence of the following diatomic molecules in ordinary flames CH, OH, $C_2$. A study of the OH absorption spectra in highly heated water vapour [46] has disclosed the importance of OH, hitherto neglected in the equilibrium $2\ H + O_2 \rightleftharpoons 2\ H_2\ O$.

From the examples given above the importance and usefulness of the applications of the study of spectra to chemistry may readily be judged. Furthermore, there is another important aspect to the question, namely, that the study of spectra, embodied in the wave mechanical and quantum mechanical theories of electrons, atoms and the interaction of atoms, has given rise to developments which have caused a marked change in our physical ideas. Already this change has been felt in chemistry and time only will tell to what extent it may take place.

An entirely different aspect of photochemistry, namely, its practical application will now be considered. The photochemical phenomenon of carbon assimilation by plants, which makes life possible on this planet, is responsible for our vast reserves of coal, oil and wood. The applications of photochemistry to industry are very numerous. For example, ultra-violet radiation is used in the halogenation of aromatic compounds, in the preparation of artificial vitamins or their equivalents, in the sterilization of potable water and milk, in testing the fastness of dyes, ink and other pigments, in the manufacture of synthetic rubber, in the drying of oils and varnishes, in the preparation of bases for varnishes, in the curing of tobacco, in the great photographical industries and many others.

# INTRODUCTION TO THE PHOTOSYNTHESIS OF HYDROGEN CHLORIDE

There are a number of factors which make this reaction of great importance as a study in photochemistry. In the first place it is the most photosensitive reaction known. Hydrogen and chlorine may remain for many months in the dark without detectable reaction, but, less than a second's exposure to bright sunlight is sufficient to cause an explosion. In the second place, it is a chain reaction, the understanding of the mechanism of which, would be of considerable theoretical value to the study of thermal chain reactions and chemical kinetics in general. In the third place, it shows an induction period, sensitivity to inhibitors, marked wall effects and a number of other peculiarities of interest to the student of kinetics. Finally, from the photochemical point of view, it exhibits an apparent photochemical threshold within an absorption band. This gives one an opportunity of studying the important question of the dependence of the quantum yield on the wave length, as well as a still more interesting question, namely, the temperature coefficient of the quantum yield. Many other points of interest to the photochemist and student of kinetics will become apparent throughout the discourse.

Of the various factors mentioned above the temperature coefficients of the light absorption and the quantum yield were of special interest to the author because these data give the answer to the following question. Is it possible that quanta too small to become effective at a given temperature, may succeed in activating molecules already partially activated by an increase in temperature? Experimental data on this question of fundamental importance to photochemistry are almost entirely lacking. The need for such information has been repeatedly emphasized by Hinshelwood and the authors of the most recent works on photochemistry (Kistiakowsky [47], Griffith and McKeowen [48] Style [49] and Dhar [50]).

Finally, another aspect of the study of the photosynthesis of hydrogen chloride which is of considerable importance is the industrial application. It is granted that very little use has been made of the reaction of chlorine with hydrogen, but, the great photosensitivity of this reaction has led to its application for the removal of hydrogen in the electrolytic production of chlorine. This process is carried out by passing the gases through a tube, irradiated by a powerful mercury arc, the hydrogen being thus converted into hydrogen chloride which is scrubbed out with water. Closely associated with this reaction are the numerous photo-haloginations of organic compounds. The patent literature contains many examples of such applications and their number is increasing year by year. Among the products which have been successfully halogenized are gasoline, petroleum oils, benzene, toluene, hydrocarbon in the vapour state, shale oil and many others.

In reviewing this literature, two very important facts stand out, namely, the great diversity of opinion and the extraordinarily little really exact and reliable information that has been recorded.

Before attacking such complex problems as these industrial processes, it is clearly necessary to deal with the simpler phenomena first. Therefore the understanding of the mechanism of the photosynthesis of hydrogen chloride is of fundamental importance.

## References. (I)

1. Beutler and Polanyi, Z. physik. Chem., B, <u>I</u>, 3(1928).
2. Bogdandy and Polanyi, ibid., B, <u>I</u>, 21 (1928).
3. Polanyi and Schay, ibid., B, <u>I</u>, 30 (1928).
4. Ootukay and Schay, ibid., B, <u>I</u>, 62 (1928).
5. Bodenstein and Lind, ibid., <u>57</u>, 168 (1906).
6. Bodenstein and Lütkemeyer, ibid., <u>114</u> 208 (1924).
7. Bodenstein, ibid., <u>29</u>, 295 (1899).
8. Ciamician and Silber, Ber., <u>36</u>, 1582 (1903).
9. Taylor, J. Phys. Chem., <u>28</u>, 984 (1924).
10. Bodenstein and Jost, J.A.C.S., <u>49</u>, 1416 (1927).
11. Lewis, J. Phys. Chem., <u>32</u>, 270 (1928).
12. Hinshelwood, Chem. Soc. Ann. Reports (1927).
13. Bodenstein, Z. physik. Chem., <u>85</u>, 329 (1913).
14. Pauli, Z. Physik., <u>31</u>, 765 (1924).
15. Heitler and London, Z. physik. Chem., <u>44</u>, 455 (1927).
16. London, ibid., <u>46</u>, 455 (1928).
17. Heitler, Z. Physik., <u>31</u>, 185 (1930).
18. Turner, Phys. Rev., <u>27</u>, 397 (1926).
19. Pringsheim, Z. Physik., <u>5</u>, 130 (1921).
20. Mecke, Ann. Physik., <u>71</u>, 140 (1923).

21. Kuhn, Z. Physik, 39, 77 (1926).

22. Eliot, Proc. Roy. Soc., A. 127, 638 (1930).

23. Eliot, Proc. Roy. Soc., 123, 629 (1929).

24. Nakamura, Mem. Coll. Sci. Imp. Univ. Kyoto, 9, 315 (1926).

25. Berge and Sponer, Proc. Nat. Acad. Sci., 13, 100 (1927).

26. Berge, Proc. Nat. Acad. Sc., 14, 12 (1928).

27. Witmer, ibid., 12, 238 (1926).

28. Giauque, J.A.C.S., 52, 4808 (1930).

29. Giauque and Johnston, J.A.C.S., 51, 1436, (1929).

30. Babcock, Proc. Nat. Acad., Sc., 15, 471 (1929).

31. Giauque and Wiebe, J.A.C.S., 50, 101, 2193 (1928).

32. Sugiura, Zeit. f. Phys., 45 484 (1927).

33. Wang, Phys. Rev., 31, 579 (1928).

34. Davisson and Germer, Phys. Rev., 30, 705 (1927).

35. Thomson, G.P. Proc. Roy. Soc., A 117, 600 (1928).

36. Knauer and Stern., Z. physik Chem., 53, 779 (1929).

37. Estermann and Stern, ibid., 61, 95 (1930).

38. Dempster, Nature, 125, 51, 741 (1930).

39. Johnston, Physic. Rev., [1] 31, 1122 (1928).

40. Johnston, J. Franklin Inst., 207, 629, 639 (1929).

41. Hinshelwood, The Kinetics of Chemical Change in Gaseous Systems, second edition 1929, Oxford Clarendon press.

42. Stuart, Z. Physik, 32, 262 (1925).

43. Gaviola, Phys. Rev., (2) 33, 309 (1929).

44. Barter, J. A.C.S., 52, 3920 (1930).

45. Mannkopf, Z. Physik, 36, 315 (1925).

46. Bonhoeffer and Reichhardt, Z. physik. Chem., A 139, 75 (1928).

47. Kistiakowsky. Photochemical Processes, First edition, 1928, The Chemical Catalogue Company, Inc.

48. Griffith and McKeowin, Photoprocesses in Gaseous and Liquid Systems, first edition, 1929, Longmans, Green and Co.

49. Style, Photochemistry, First edition, 1930, Methuen and Company Limited.

50. Dhar, The Chemical Action of Light, First edition, 1931, Blackie and Son Limited.

# SECTION II.

# HISTORICAL

## 1. Photochemistry

Photochemistry is a comparatively young science. Although a number of investigators since the days of Aristotle have reported occasional observations, only in the 19th century was the first fundamental law enunciated.

The influence of light on the formation of the green colour in plants and its bleaching in the dark were first recorded by Aristotle, (384 B.C.). Vitruvius (30 B.C.) noted that certain naturally occurring dyes were bleached by sunlight. Some of the writings of the alchemists contain vague references to the action of light.

The empirical study of the effect of light began at the end of the 17th century with the observation of Ray, a botanist, of the action of light on plant growth. Not long after this Bestucheff noted that sunlight could discharge the colour of a solution of ferric chloride in alcohol. Hales (1677 - 1721) a contemporary of Newton, was probably the first to suggest the influence of light on plant nutrition, the theory of which was later explained by Priestley..

In 1727 Schultze, a German physician, accidently discovered that silver carbonate was photo-sensitive. It is true that previous to this Boyle had noted the blackening of silver chloride on exposure to light but he attributed it to action of the air.

At the beginning of the 19th century two discoveries were made which were destined to have a profound influence on the future of photochemistry. The first, was that of Cruickshank in Nicholson's Journal,[1] who noted the effect of light on a mixture of hydrogen and chlorine, The decomposition of chlorine water by light had been previously discovered by Berthollet and the first actinometer built by de Saussure (1790) utilizing this discovery. The second notable discovery was that of Ritter [2] who found that with spectrally dispersed light certain invisible rays, more refrangible than violet, darkened silver chloride. This marked the discovery of the existence of ultra-violet light. At the same time in explaining the different action of red and violet rays on the luminescence of phosphorus, he stated that the violet belonged to the reducing and the red to the oxidizing part of the spectrum. This statement of a "chemical polarity" of the spectrum therefore preceded the enunciation of Grotthus's[3] photo-chemical principles and must be regarded as the first photochemical generalization.

Then followed a number of investigations on the photochemical reaction of chlorine by, Davy, Faraday, Gay - Lussac, Thenard, Seebeck, Favre and Silbermann and Dalton.

A great impetus was given to the study of photochemistry by Grotthus [3] who in 1818 endeavoured to combine the known facts of photochemistry in generalizations based in the electrochemical theories of Davy and Berzelius. The most important of these was his absorption law, which was simply a recognition of the fact that absorption of some part of the light incident on a system is a necessary preliminary to photochemical change in the system.

Very little attention was paid to Grotthus and a quarter of a century later the same law was rediscovered by Draper [4] and supported by experimental evidence based on the hydrogen-chlorine reaction. His tithonometer as he called it was simply a bulb containing water, connected to a capillary tube which measured the contraction, due to the solution of the hydrogen chloride formed, by movement of water along the capillary. Among the observations made were the following; on first illumination there was a ten minute induction period, followed by an increase in velocity to a constant value, the indigo rays being most effective.

The next important advance was the work of Bunsen and Roscoe [5] in an improved technique. Among a number of observations which have since been contradicted, they observed that 0.5 per cent oxygen decreased the sensitivity ten times, that reaction velocity was directly proportional to the light intensity over a four-fold range and that Beer's law held over a considerable pressure range.

During the remainder of the 19th century very little progress was made in the theoretical development of photochemistry, the successful development of the practical side of photography commanding all the attention.

Then came the quantum theory and its application to photochemistry by Einstein in 1905.[6-10] The great stimulus to research came with his enunciation in 1912 of the photochemical equivalence law. This stated qualitatively says, that in a photochemical reaction, one quantum of active light is absorbed per molecule of absorbing and reacting substance which disappears. It was through the large number of experimental investigations carried out to test the validity of this law that the real progress in photochemistry was made. Of course the law as above stated is true only in a few cases, the key to the situation being suggested by Stark in two papers[11,12] four years before the Einstein law was enunciated. In these papers are to be found, sometimes explicitly stated, sometimes only inferred, not only the photochemical equivalence relation, but also a clear distinction between the primary and secondary stages of a photochemical reaction including sensitized reactions. Stark's views did not receive the attention they deserved possibly because they were put forward incidentally in papers dealing with other subjects and were clothed in qualitative language and not given the dignity of a thermodynamic deduction.

In any discussion of the photochemical equivalence law, a sharp distinction must be drawn between the physical and chemical fulfilment of it. When an isolated molecule absorbs a quantum, the formation of an excited molecule or its dissociation is the invariable result and thus limited the law appears to be absolutely valid. Its chemical validity however, depends on the chemistry of the succeeding processes, which in turn depend upon a number of factors both chemical and physical. These may reduce the chemical yield far below the theoretical value of unity or raise it to some higher value. This point was clearly recognized by Stark[13].

The quantum efficiency ($\gamma$) or quantum yield is usually defined as the number of molecules which react per quantum of light absorbed. The number of reactions found with a ($\gamma$) close to unity is rather surprising.[14] Most of the work done to test this point has been carried out in the laboratories of Allmand, Berthelot, Bodenstein, Chapman, Ciamician, Dhar, Franck, Luther, Nernst, Warburg, Weigert, Winther and others. During the last decade the application of spectral evidence has become appreciated and a new impetus has been given to photochemistry. At the present time photochemists are awaiting eagerly the development of the new quantum mechanical resonance principle, which should have a very wide application.

## 2. The Photosynthesis of Hydrogen Chloride

It is already apparent from the discussion presented above that the early quantitative study of photochemistry was really a study of the hydrogen-chlorine reaction. A repetition of this work will not be given here. In the following section, in order to simplify the discussion of the evidence bearing on the above reaction, the historical account will be broken up into sections dealing with different phases of the problem.

### The Induction Period.

Van't Hoff was of the opinion that the phenomenon of the induction period was not due to a specific photochemical effect, but, rather due to some imparity, a view which is accepted to-day. A great deal of the early work was carried out to study this phase of the reaction which is now considered to be of incidental significance.

To Burgess and Chapman [15] must be given the credit for clearing up this phenomenon after a century of effort by a large number of very able experimenters. They showed, as a result of exhaustive tests, that it was due to traces of impurity present in chlorine gas or the actinometer liquid, or in the stopcock grease or on the walls. They also showed that the inhibitor could be destroyed by chlorine either photochemically or by heating for some time at 100°. It was found that the usual inhibitor was nitrogen trichloride formed from ammonia dissolved in the water and the chlorine. Five cc. of a solution containing slightly less than 1/1000 of a milligram of ammonia gave an induction period of almost two hours, the length of the period varying directly as the ammonia concentration.

Certain other substances were also found to have an inhibiting effect, ozone, chlorine dioxide, nitric oxide and egg albumen. .022 grams of the latter substance gave an induction period of one hour due probably to liberation of ammonia. On the other hand alcohol, ether, benzene, sulphur dioxide, nitric acid, stannous chloride, hydrogen peroxide, potassium permanganate and aqua regia produced no inhibiting influence. Burgess and Chapman have taken special precautions to eliminate the above mentioned inhibiting impurities and after a great deal of controversy their conclusion appears to be accepted, namely, that the induction period is really due to the time required to destroy some impurity before the hydrogen and the chlorine can unite directly. Chapman[16] estimated that the sensitivity of an hydrogen chlorine mixture is reduced at least one hundred-fold by the presence of one molecule of nitrogen trichloride in $10^6$ molecules of $[H_2 + Cl_2]$

The Budde Effect.

In 1871 Budde[17,18] observed that when chlorine was exposed to sunlight a considerable expansion was obtained, which was not given if a piece of red glass was interposed. With a dark blue filter the expansion was two thirds of that obtained with direct sunlight. Mellor[19] and Bevan[20] showed that the expansion was quantitatively accounted for by the rise in temperature due to the heating effect of the absorbed light. Richardson[21] confirmed the experiments of Budde. On the other hand Shenstone[22] obtained no Budde effect in carefully purified chlorine which had been dried over phosphorus pentoxide for four months. Baker[23] also mentions that he found no Budde effect with dry chlorine but he does not discuss any experiments.

Experiments by Le Blanc [24], Halban and Siedentopf[25], Kornfeld and Steiner[26], Cole[29] and Kistiakowsky[28] on the absorption and scattering of wet and dry chlorine, failed to detect any difference between the two. Finally, both Martin [29] and Kistiakowsky [30] recently found that the Budde effect was unaffected by quite extensive drying although not in the "Bakerian" sense.

The Draper Effect.

Draper [4] observed that when a mixture of ($H_2 + Cl_2$) was irradiated in his tithonometer, he obtained a period of brief expansion followed by a period of no pressure change and finally a contraction. The expansion was explained by a heating effect, due to the contraction of hydrogen and chlorine, and was called by Mellor the Draper effect [31]. Also by increasing the intensity of the light, the expansion could be increased in magnitude until an explosion occurred.

Weigert and Kellerman [32] examined the Draper effect in detail and showed that the expansion was thermal in origin and could be calculated quantitatively from the amount of hydrogen chloride formed. In their investigation the Töpler cloud method was used, by which an instantaneous register could be obtained of the effect of light during the initial part of the reaction. This was done by photographing the local changes in refractive index. They regarded their results as direct evidence of a chain reaction. Using an intense spark of short duration they demonstrated that this reaction did not proceed instantaneously, but required a measureable time for completion. This effect has very little in common with the induction period already discussed since it is of a quite different order of magnitude. Weigert concluded from the observed period of 0.01 seconds and a calculated quantum yield of $10^5$ molecules that a chain mechanism was taking place each atomic process requiring $10^{-7}$ seconds.

More recently the Draper effect has been studied by Horiba and Ichikawa [33] and Ichikawa [34] using a new method in which the actual changes in pressure due to this effect were recorded on a photographic film. By this method a direct measure of the extent of the Draper effect from 1/120th of a second after exposure to two seconds is given.

## The Role of Water Vapour in the Hydrogen-Chlorine Reaction.

The hydrogen-chlorine reaction is one of those reactions in which the effect of water vapour plays a prominent part, the interpretation of which has been the subject of much discussion and speculation with many divergent views. That the effect of drying produces a marked inhibiting effect on the reaction has been observed by Baker [35], Mellor and Russell [36], Bodenstein and Dux [37], Coehn and Tramn [38,39], Coehn and Jung [40,41] and Coehn and Heymer [42].

The most thorough investigation is probably that of Coehn and Jung who observed that in visible light no combination took place when the pressure of the water vapour was $10^{-7}$ mm of mercury. Furthermore, they found that the rate of reaction steadily increased with the vapour pressure of water until a maximum rate was obtained at $10^{-5}$ mm of mercury. However, with ultra-violet light, reaction took place at any water vapour concentration. Norrish[43] calculated that at $10^{-7}$ mm only one hundredth of the surface was covered, while at $10^{-5}$ the whole surface could be covered with a layer one molecule thick. Norrish postulated that the reaction was initiated in the surface layer of water on the walls. Coehn and Heymer found the quantum yield in the dry gases to be only 7 in ultra-violet light.

## The Effect of Oxygen.

The inhibiting effect of oxygen first observed by Bunsen and Roscoe[5] has been verified by all subsequent experimenters. Along with the photosynthesis of hydrogen chloride in an hydrogen-chlorine-oxygen mixture, a sensitized formation of water takes place. Fortunately the extent of this reaction is small, even with two per cent of oxygen present, so that the concentration of the inhibitor remains sensibly constant. The rate of photosynthesis when the light is kept constant is a function of the relative concentrations of hydrogen, chlorine and oxygen. Roughly speaking the rate is inversely proportional to the oxygen pressure.

With regard to the question of removal of oxygen, it should be emphasized, that it is only within the last few months that any experimenter has worked with mixtures of hydrogen and chlorine completely freed of oxygen, i.e. (1 part in ten million). Bodenstein[75] using very elaborate precautions claimed he had an oxygen free system. Since traces of oxygen exert an appreciable inhibiting effect, it is not unlikely that its presence in varied concentration has been responsible for a considerable lack of agreement in experimental facts.

## The Effect of Light Intensity.

All investigations on this point, with the exception of that of Baly and Barker[45] have led to the conclusion that the velocity of reaction was directly proportional to the light intensity. Baly found that the rate was proportional to a power of the intensity greater than unity. Only one other similar case for any photochemical reaction has been recorded in the literature

(Wood [46]).

The chief workers on this question were Draper [4], Bunsen and Roscoe [5], Chapman [47], Baly and Barker [45], Marshall [48], Kornfeld and Müller [49] and quite recently Allmand [50]. The latter investigator found direct proportionality up to a range of 1:440 at 436 m μ as compared with the greatest previously studied range of Kornfeld and Müller (1:64).

## Life of the Activated Chlorine and the Effect of Walls.

Le Blanc and Volmer [51] and Bodenstein and Taylor [52] showed that following an interval of .001 - .0015 of a second after illumination, no hydrogen chloride was formed when an illuminated stream of chlorine was passed through a bent capillary tube into hydrogen. Gohring [53] analyzed the results and showed that under the experimental conditions the amount of hydrogen chloride produced would be too small for detection, i.e. .00065 of a second after illumination. The same negative result was obtained by Wendt, Landauer and Ewing [54] for an interval of 0.01 of a second using an intense mercury vapour arc. Marshall [55] also tried the same experiment using an improved technique. In his work greater precautions were taken to remove inhibitors and purer chlorine was used but no reactivity was observed after 0.0003 seconds of intense illumination.

Coehn and Heymer [56] directed a jet of $[H_2 + Cl_2]$ from a capillary into a U tube immersed in liquid air. A narrow beam of light was concentrated on the stream far from any glass surface, so that only a homogenous reaction could take place. In spite of the fact that the U tube was open to the air considerable formation of hydrogen chloride took place without the presence of walls.

Furthermore, Chapman and Grigg [57] have shown that under the same conditions of illumination, the velocity of the photochemical reaction between chlorine and hydrogen, in capillary tubes is considerably less than in wider tubes. The result has been explained by the hypothesis that the union of the gases is due to an unstable catalyst which is formed by light and is destroyed when it comes into contact with glass.

A more extensive experiment has been carried out by Trifonov [58], and Trifonov and Rjabinin [59] to study the effect of walls. They found, that in cylindrical vessels of varying diameters, the quantum yield was proportional to the square of the diameter for low pressures (about 10 m m total) but was independent of the dimensions above 30 m m. They also observed that above 0.2 m m pressure, the velocity of the reaction was proportional to the cube of the pressure, in agreement with Semenov's [60] calculations. Below this pressure the reaction either ceased or proceeded very slowly.

## Absorption of Light by Chlorine.

The absorption spectrum of chlorine has been investigated by the following; Laird [61], Ribaud [62], Dobbie and Fox [63], Turher [64], Kuhn [65], Nakamura [66] and more recently by Eliot [67,68]. The results of these investigations show that at ordinary temperatures an appreciable band spectrum begins at 5800 A°. This increases in intensity more or less regularly until it changes to a continuous spectrum at the convergence limit 4785 A°. Over fifty band edges have been examined.

The extinction coefficients have been determined by Weigert and Nickolai [69], Halban and Siedentopf [70] and Gray and Style [71]. The most accurate and complete study was made by Halban and Siedentopf. They measured the absorption over the range 2540 - 6430 Å for 31 lines, using a monochromator and two photoelectric cells balanced so as to compensate for any change in the intensity of the light source. For the light source mercury zinc and cadmium arcs and a nitra lamp was used. From the results it was found that within the pressure limit, 760 mμ downwards, Beer's Law held. The absorption curve showed a maximum in the ultra-violet at 3340 Å and a minimum in the yellow at 5791 Å. From the yellow to the red the absorption again increases reaching a maximum at about 6140 Å. No difference was observed between dry and moist chlorine.

Weigert and Nic~~h~~olai reported that the absorption of chlorine was dependent on the incident intensity and varied inversely as the intensity, thus disagreeing with the results of Halban and Siedentopf, discussed above. A special investigation to examine this point was made by Gray and Style. Their results were in complete accord with those of Halban and Siedentopf.

Quantum Yield.

Bodenstein [72] was the first to investigate the quantum yield or the number of molecules of hydrogen chloride formed per quantum of light absorbed. He calculated a yield of $10^6$ molecules of hydrogen chloride per quantum but later work showed this estimate to be two or three times too high. The first accurate determination of the quantum yield was made by Kornfeld and Müller[73]. The maximum which they could obtain was $1.10 \times 10^5$ at $\lambda$ 436 m$\mu$, at an estimated oxygen concentration of about 0.01%. Marshall studied the effect of low pressures on the quantum yield and found that at 60 m m total pressure it was 20,000 and at 0.01 m m total pressure only 20. He used total light from a mercury lamp, calculating the average wave-length from the spectral distribution. From this the average extinction coefficient of chlorine, he estimated the approximate quantum yield. Heymer obtained a yield of 7500, 2000 and 7000 at 436, 265, 254 m$\mu$ respectively.

Up to this point no one had obtained the quantum yield using a very low concentration of oxygen. However recently Harris [76] succeeded in obtaining a very large quantum yield using a mixture with an estimated oxygen concentration of the order of 1 part in 100,000. He calculated a value of $6 \times 10^5$ as a maximum limit, but stated that the actual yield might well be ten times as great. To remove the last traces of oxygen from the chlorine he passed a current of hydrogen through liquid chlorine continuously for a period of six weeks.

Following up the work of Harris, Bodenstein and Unger[75] made an attempt to obtain an oxygen free mixture. Their chlorine was treated as above but all the hydrogen used was put through a palladium valve. As mentioned before their oxygen concentration was estimated at 1 part in 10,000,000. Previously Cremer[77] had calculated that under these conditions the yield should reach $7.6 \times 10^6$ . On the other hand Bodenstein and Unger[75] found experimentally a yield of $1.1 \times 10^5$ at $\lambda$ 436 m$\mu$.

All the investigations mentioned so far regarding the quantum yield have been carried out using the Bodenstein technique with very carefully purified gases and with no stopcock grease or water.

Several investigations have been using the Bunsen and Roscoe technique. Lind and Livingston[78] claim a yield $10^5$, although most of their work was carried out with sensitivities of about 80,000. On the other hand, Allmand and Beesley[50] obtained a yield of only 250,000.

## Photochemical Threshold.

A number of workers have reported a photochemical threshold as follows: Padoa and Butironi[79] 550 mμ; Taylor[80] 490; Taylor and Eliot[81] 600; Coehn and Jung[40,41] 540; Weigert and Nicholai[82] 590; and Allmand and Beesley 546[50].

## Temperature Coefficient.

The present data on the thermal temperature coefficient are rather unsatisfactory, the most reliable being that of Sirk[83]. In discussing this question Hinshelwood[84] has expressed the following opinion. "Only fragmentary information is available about the thermal union of hydrogen and chlorine, nearly all investigators having confined their attention to the photochemical reaction. The matter is in need of further investigation".

By photochemical temperature coefficient is meant the ratio of the amounts of hydrogen chloride produced in a given time, per 10 degrees rise in temperature, by light of constant intensity. Observations on this coefficient have been reported by the following; Bewan [85], Padoa and Butironi [86], Porter Bardwell and Lind [87], Lind and Livingston [78], Allmand and Beesely [50] and Bodenstein [75]. Their results vary from 1.16 to 1.61 depending on wave-length and temperature interval. As a complete discussion of the results will be presented later the details will not be given here. However, it is interesting to note that in spite of the possible complications, the Arrhenius equation holds remarkably well for Bodenstein's results and at least approximately for those of the others.

It is also of considerable significance to note that Lind and Livingston [78] found the ratio of the quantum yield (white light) to the yield per ion pair, produced by $\alpha$ particles, to be unity and to have identical temperature coefficients.

The photochemical temperature coefficient is probably the algebraic sum of three other temperature coefficients, namely, the temperature coefficient of the light absorption, the primary process and the secondary. The temperature coefficient of the quantum efficiency being the temperature coefficient of the primary activation process plus the temperature coefficients of the succeeding reactions in the thermal chain.

### Temperature Coefficient of the Light Absorption and Quantum Yield.

There is practically no quantitative data on either of these very important points. Dobbie and Fox[63] have shown that the continuous region in the absorption spectrum of chlorine extends towards the red as the temperature is increased. Kuhn[65] observed that certain progressions in the band spectrum increased in intensity with rise in temperature.

Up to the present time no experimental data exist regarding the temperature coefficient.

## The Kinetics and Mechanism of the Reaction.

In the above historical sketch it has only been possible to mention the more important investigations. In order to avoid repetition many isolated bits of experimental evidence will be cited later in the discussion. Furthermore, no mention has been made of the many contraversies both of historical and contemporary importance and in most cases experimental evidence which has later been disproved has been omitted.

It is only natural that a great number of theories have been put forward to explain different phases of the work, many of which are based on scanty experimental evidence. It would take many pages to review these theories. Moreover, the very thorough investigation of Bodenstein and Unger [75], carried out a few months ago, has added further complications. As a result of this work most of the current so-called theories will require considerable modification.

The theories of the mechanism of this reaction may be divided into two general classes. 1. The activated molecule type proposed by Bodenstein [88] in 1916. 2. The atom chain theories first proposed by Nernst [89,90]. Numerous equations based on these theories have been derived to express the velocity in terms of the light intensity, partial pressures of hydrogen, chlorine, oxygen, hydrogen chloride, water etc. The most important of these equations are those of Gohring [91], Cremer [77], Chapman [92], Thon [93], Bodenstein and Dux [37] and Bodenstein and Unger [75].

Unfortunately for the simplification of any mechanism, water plays an important role in its development. The theories of the mechanism of the action of water vapour, based on the experimental evidence given above, may be roughly classified under five headings, the distinction being made by the point at which water enters into the process. Theories in which

1. The action of water modified the primary process of absorption of light (Weigert [69], Thon [93], Lewis [94], and Rideal [95].)
2. A definite chemical reaction is supposed to take place at some step in the process before

the actual chain mechanism begins (Stern and Volmer [96] and Chapman [97]).

3. Water is one of the reactants in the chain part. (Coehn and Heymer [42]).
4. Water is supposed to influence certain stages of the chain mechanism due to a large stray field of force or collision diameter (Cathala [98] and Kornfeld [99]).
5. A heterogenous reaction at the surface of the cell is assumed (Bowen [100] and Norrish[101]).

When it is remembered that the wave-length of the light, the temperature, the dimension, composition and previous history of the reaction cell, all may quite possibly modify or change a given mechanism, it is readily seen how difficult any general interpretation of the results may become.

It is no wonder that Hinshelwood [102] called it the Mona Liza of chemical reactions or that Bodenstein who did his first work on it eighteen years ago began his latest paper with the following sentence "Die photochemische Kinetik des Chlorknallgases ist ein unerschöpfliches Thema; trotz aller aufgewandten Mühe ist sie von eihigermassen, vollstandiger Klarstellung noch weit entfernt. [75]

## References (II)

1. Cruickshank, Nicholson's Journal[1] 5, 202 (1801).
2. Ritter, Beiträge zür Kenntniss der Galvanismus, 2, 282, (1802).
3. Grotthus, Ostwalds' Klassiker, Nr 152, p. 101.
4. Draper, Phil. Mag., 25, 1 (1844).
5. Bunsen and Roscoe, Ostwalds' Klassiker, 34 and 38.
6. Einstein, Ann. Physik.,[IV] 17, 132 (1905).
7. Einstein, ibid., [IV] 37, 832 (1912).
8. Einstein, ibid., [IV] 38, 881 (1912).
9. Einstein, ibid., 38, 881 (1913).
10. Einstein, Ber. Deutsch physik. Ges., 18, 315 (1916).
11. Stark, Physik. Z., 9, 889, 894 (1908).
12. Stark, Prinzipien der Atomik Dynamic, (ii) 207 (1911).
13. Stark, Physik. Z., 9, 898 (1909).
14. Griffiths and McKeown, Photoprocesses in Gaseous and Liquid Systems, 1st edition, 1929, Longmans, Green and Co.
15. Burgess and Chapman, J. Chem, Soc., 89, 1399 (1906).
16. Chapman, Science Progress, 25, 72 (1917).
17. Budde, Phil, Mag., (4) 42, 290 (1871).
18. Budde, Pogy. Ann., 6, 477 (1873).
19. Mellor, J. Chem. Soc., 81, 1289 (1902).

20. Bevan, Phil. Trans., 202, 90 (1904).

21. Richardson, Phil. Mag., 277, (1891).

22. Shenstone, J. Chem. Soc., 71, 471 (1897).

23. Baker, Brit. Assoc. Reports, 496 (1894).

24. LeBlanc, Z Elektrochem., 25, 234 (1919).

25. Halban and Siedentopf, Z. physik. Chem., 103 71 (1922).

26. Kornfeld and Steiner, Physik Z., 45, 325 (1927).

27. Cole, Trans. Amer. Electrochem. Soc., 49, 135 (1926).

28. Kistiakowsky, J.A.C.S., 42, 2194 (1927).

29. Martin, Cole and Lent, J. Phys. Chem., 33, 148 (1929).

30. Kistiakowsky, J.A.C.S., 51, 1395 (1929).

31. Mellor and Anderson, J. Chem. Soc., 81, 414 (1902).

32. Weigert and Kellerman, Z., physik. Chem., 107, 1 (1924).

33. Horiba and Ichikawa, Sexagint Osaka Celebration Kyoto, 73, (1927).

34. Ichikawa, Z. physik. Chem., 10, 299, (1930)

35. Baker, J. Chem. Soc., 65, 611 (1894).

36. Mellor and Russell, ibid., 81, 1272 (1902).

37. Bodenstein and Dux, Z. physik. Chem., 85, 297 (1913).

38. Coehn and Tramm, ibid., 105, 356 (1923).

39. Coehn and Tramm, Ber., 56, 458 (1923).

40. Coehn and Jung, Z. physik. Chem., 110, 705 (1924).
41. Coehn and Jung, Ber., 56, 696 (1923).
42. Coehn and Heymer, Naturwiss., 14, 299 (1926).
43. Norrish, Trans. Faraday Soc., 21, 575 (1926).
44. Chapman and MacMahon, J. Chem. Soc., 95, 959 (1909).
45. Baly and Barker, J. Chem. Soc., 119, 653 (1921).
46. Wood, Phil.Mag., 43, 757 (1922).
47. Chapman, J. Chem. Soc., 125, 1521 (1924).
48. Marshall, J. Phys. Chem., 29, 1453 (1925).
49. Kornfeld and Müller, Z. physik. Chem., 117, 242 (1925).
50. Allmand and Beesly, J. Chem. Soc., 2693 (1930.
51. LeBlanc and Volmer, Z Elektrochem., 20, 494 (1914).
52. Bodenstein and Taylor, ibid., 22, 202 (1916).
53. Gohring, ibid., 27, 516 (1921).
54. Wendt, Landauer and Ewing, J.A.C.S., 44, 2377 (1922).
55. Marshall, J. Phys. Chem., 30, 757 (1926).
56. Coehn and Heymer, Ber., 59, 1794 (1926).
57. Chapman and Grigg, J. Chem. Soc., 3233 (1928)
58. Trifonov, Z. physik. Chem., B, 3 , 195 (1929).
59. Trifonov and Rjabinin, ibid., 6, 118 (1929).

60. Semenov, Z. physik, 48, 571, (1928).

61. Laird, Astroh. Phys. J., 14, 85 (1901).

62. Ribaud, Ann. physique, 12, 107 (1919).

63. Dobbie and Fox, Proc. Roy. Soc., A 99, 456 (1921).

64. Turner, Phys. Rev., 27, 397, (1926).

65. Kuln, Physik. Z., 39, 77 (1926).

66. Nakamura, Mem. Coll. Sci. Imp. Univ. Kyoto, A 9 315 (1926).

67. Eliot, Proc. Roy. Soc., A 123, 629 (1929).

68. Eliot, ibid., 127, 638 (1930).

69. Weigert and Nicholai, Z. physik. Chem., 131, 267 (1928).

70. Halban and Siedentopf, ibid., 103, 71 (1922).

71. Gray and Style, Proc. Roy. Soc., A 126, 603 (1930).

72. Bodenstein, Z. physik. Chem., 85, 351 (1913).

73. Kórnfeld and Müller, ibid., 117, 242 (1925).

74. Heymer, Diss., (Göttingin) 1927.

75. Bodenstein and Unger, Z. physik. Chem., 11, 293 (1931).

76. Harris, Proc. Nat. Acad., 14, 110 (1928).

77. Cremer, Z. physik. Chem., 128, 285 (1927).

78. Lind and Livingston, J.A.C.S., 52, 593 (1930).

79. Padoa and Butironi, Atti. R. Dioad. Lincei, 25, 215 (1916).

80. Taylor, Phil. Mag., VI, 49, 1165 (1925).

81. Taylor and Eliot, Trans, Faraday Soc., 23, 583 (1927).

82. Weigert and Nicolai, Trans. Faraday Soc., 23, 583 (1927).

83. Sirk, Z. physik. Chem., 61, 543 (1908).

84. Hinshelwood, Kinetics of Chem. Change in Gaseous Systems, 2nd edition, P. 83, 1929 Oxford Clarendon press.

85. Bewan, Proc. Camb. Philos. Soc., 12, 398 (1904).

86. Padoa and Butironi, Gazz. Chem. Italiana, 47, 6 (1917).

87. Porter, Bardwell and Lind, J.A.C.S., 48, 2603 (1926).

88. Bodenstein, Z. Elektrochem., 22, 58 (1916).

89. Nernst, ibid., 22, 62 (1916).

90. Nernst, ibid., 24, 335 (1918).

91. Gohring, ibid., 27, 511, (1921).

92. Chapman, J. Chem. Soc., 123, 3079 (1923).

93. Thon, Z. physik. Chem., 124, 327 (1926).

94. Lewis, Trans. Faraday, Soc., 21, 584 (1926).

95. Rideal, J.A.C.S., 48, 2553 (1926).

96. Stern and Volmer, Z. wiss. Phot., 19, 275 (1920).

97. Chapman, Trans. Faraday, Soc., 21, 547, (1926).

98. Cathala, Compt. rend., 181, 33 (1925).

99. Kornfeld, Z. physik. Chem., 131, 97 (1927).

100. Bowen, J. Chem. Soc., 125, 1233 (1924).

101. Norrish, J. Chem. Soc., 127, 2317 (1925).

102. Hinshelwood, Chem. Soc., Ann. Reports (1927).

## SECTION 111

## PURIFICATION AND STORAGE OF MATERIALS

### 1. Introduction.

It may readily be seen from the above historical sketch that the purification of materials plays a very important part in any investigation on the photosynthesis of hydrogen chloride. The lack of proper precautions in the past is responsible for a vast number of conflicting observations.

It was decided in the present work, not to attempt a complete removal of oxygen from the gases as this was not practical from the point of view of time and equipment. For example, to remove completely the oxygen from hydrogen, Bodenstein and Unger[1] found it necessary to use a palladium valve. For the complete removal of the oxygen from chlorine they first fractionally distilled the gas in vacuo using liquid air. Following this pure hydrogen was bubbled continuously through the liquid chlorine for a period of six weeks. In the present investigation, although the gases were not completely freed of oxygen, precautions were taken to keep the composition of the various chargings of the reaction cell as nearly alike as possible.

The gases are purified in the same manner for both the Bunsen-Roscoe and Bodenstein Techniques, the methods of charging the cells however being slightly different.

## 2. Purification of the Chlorine.

When employing the Bunsen-Roscoe Technique, it has been the custom in the past to use the products of the electrolysis of hydrochloric acid, obtained with platinium-iridium or carbon electrodes. These gases are passed through a bubbler into the reaction cell. Of course, the electrolysis introduces oxygen, the concentration of which in some of the more recent work was reduced by alternating the current every 5 seconds. It is possible that the oxygen being formed during the anodic pulses and absorbed by the electrode, is reduced to water by the cathodic pulse. Another source of oxygen is obtained from the decomposition of the hypochlorous acid, formed by the action of chlorine on the water in the bubbler.

When carbon electrodes are used still another source of impurity is introduced, namely carbon monoxide. This arises from the oxidation of the carbon. The carbon monoxide may in turn either be oxidized to carbon dioxide by reacting with the oxygen present in a chlorine sensitized photochemical reaction, or react photochemically to form phosgene, another well known chain reaction.

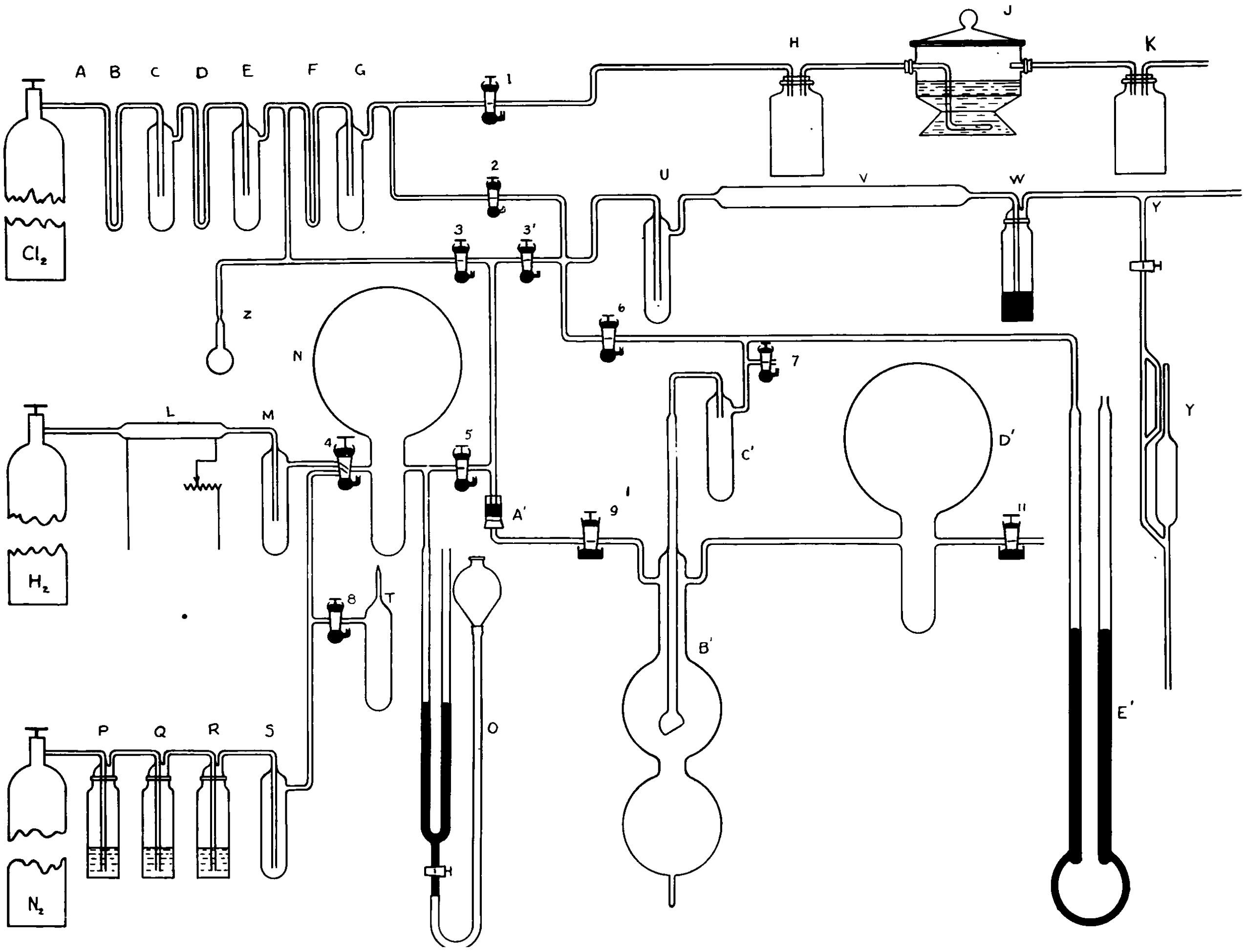
It has also been observed that when chlorine has been dried over phosphorus pentoxide, different chargings of the cell, give different rates of reaction. (Cremer,[2] Bodenstein[1].) Furthermore Melander[3] has shown that sulphuric acid has an effect on the thermal hydrogen-chlorine reaction.

In the present work, it was decided not to bubble the gas through water or sulphuric acid or to dry it over phosphorus pentoxide, but to fractionate it in vacuo using liquid air.

The usual organic stopcock lubricant being out of the question, recourse was made to an inorganic type. Two kinds were tried out. The first was one developed by Stephens[4] and the second by Boughton[5]. The second was less hygroscopic. It contained metaphosphoric acid, orthophosphoric acid and crystals of boric acid. Mercury sealed stopcocks were used to protect the lubricant. Where practical, capillary U-tubes in which chlorine could be frozen solid by liquid air were used, in place of stopcocks.

The chlorine used was taken from a cylinder of liquid chlorine. Analysis showed that it contained about 1 per cent hydrogen chloride, 0.5 per cent carbon dioxide, and a little carbon monoxide. The analysis was carried out by the usual mercury method. After the series of fractionations described below, a sample was drawn off into a 20 cc. sampling tube having the upper end drawn out into a capillary. The lower end was broken off under mercury. By this means of analysis it was estimated that the purified gas contained less than 1 part in 10,000 of impurity not absorbable in mercury.

The complete purification system for chlorine, hydrogen and nitrogen used in all experiments is shown in Fig. 1. (A) is a metal to glass seal made with sodium silicate (S.G. 1.4). The silicate was painted on with a brush in thin layers, allowing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4
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A'
9
C'
D'
11
H
Y
H₂
8
T
B'
P
Q
R
S
O
E'
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Figure I.

each coat to harden before the application of the next.

The procedure in fractionating the chlorine was as follows. After a thorough evacuation of the whole system, the valve on the chlorine cylinder was opened and a large volume frozen out in (E) with liquid air. Liquid air was then applied to (B) to block the capillary with solid chlorine. The gases not condensed were pumped off through (U,V,W,) (U) being a liquid air trap; (V) a phosphorus pentoxide tube, containing mercury as well; and (W) a mercury trap to protect the McLeod Gauge and pumps from chlorine.

Solid carbon dioxide and acetone was now applied to (E) and liquid air to (G) and the first fraction distilled into (G). By freezing (F) and opening tap 1 the discarded fraction was pumped off through (H,J,K,), (J) being a dessicator filled with sodium carbonate to absorb the chlorine. The inflow tube of (J) went to the bottom and formed a flat spiral containing a number of fine holes through which the chlorine bubbled in a number of streams, thereby increasing the absorption. After nearly all the chlorine was removed in this manner, tap 1 was closed and (G) evacuated thoroughly through (U,V,W,X and Y ). The liquid air was removed from (F) and the evacuation continued. The liquid air was applied to (E) again during this evacuation. Now, by applying the liquid air to (C) and the carbon dioxide to (E) the major fraction of the chlorine was distilled into (C), the end fraction being discarded as above. This procedure constituted one distillation.

The chlorine was distilled in the above manner three times and the purified fraction held in (C) (E) or (G) until ready for use by means of solid carbon dioxide and acetone. Samples could be drawn off into (Z) and analysed as mentioned above.

### 3. Purification of Hydrogen and Nitrogen.

The only purification that was considered necessary was the removal of the oxygen. This was accomplished by passing the gas straight from a cylinder over heated platinized asbestos in (L), the water formed being removed in (M) by means of the carbon dioxide acetone mixture. The hydrogen was stored in (N) a two liter flask and the pressure obtained by means of a mercury manometer (O).

Since it has been found that sufficient water vapour to cover the walls of the reaction cell is necessary for the hydrogen chlorine reaction, a small but constant pressure of water vapour was added to the hydrogen. This was accomplished by means of ice frozen with acetone and solid carbon dioxide.

In the case of nitrogen, as in that of chlorine and hydrogen, oxygen was the dangerous impurity. It was removed by two wash-bottles containing one of Fieser's solutions made up as follows: 13.3 gms. of sodium hydroxide were disolved in 100 cc of water and 16 gms of sodium hydrosulphite added. This solution was then added to 4 gm of sodium anthraquinone, previously weighed into the wash bottles. A third wash bottle, following the Fieser's solution and containing lead acetate solution, indicated when the oxygen solution was spent by turning black.

A liquid air trap (S) followed the above wash-bottles, to remove any condensable impurities. The nitrogen was stored with the hydrogen in (N).

## 4. Purification of Water, Mercury and Glass.

The water used in (N) was added from (T). The dissolved gases in this were removed by alternate freezing and melting in vacuo in (T). The water was then distilled at low temperature under its own pressure into (N).

The mercury used in the mercury vapour lamp was distilled three times in a current of oxygen.

All the glass that came in contact with the purified gases was first cleaned in dichromate sulphuric cleaning solution, followed by distilled water. After being placed in the apparatus the glass was heated with a flame while the system was under a high vacuum.

## 5. Mixing and Storage of Hydrogen and Chlorine.

When using the Bunsen-Roscoe Technique, the hydrogen and chlorine were mixed in $(D^1)$ and $(B^1)$ before charging the reaction cell. $(D^1)$ is a glass diaphragm manometer backed by a mercury manometer $(E^1)$. The description and method of using the diaphragm manometer are given in section IV . Mixtures with varying amounts of hydrogen and chlorine could be let into $(D^1)$ and $(B^1)$ through the taps 3, 5 and 9, the pressures being read by means of the glass manometer.

## References. 111.

1. Bodenstein and Unger, Z. physik.Chem.,11, 293(1931)

2. Cremer, Z. physik. Chem.,128, 258 (1927).

3. Milander, Mellor Comp. Treatise Inorganic and Theoretical Chamistry, Longmans Green and Company, Vol. 11, P.60 (1922)

4. Stephens, J.A.C.S., 52, 635 (1930).

5. Broughton, J.A.C.S.,30, 2813 (1930).

6. Fieser, J.A.C.S., 46, 2639 (1924).

# SECTION IV.

# THE TEMPERATURE COEFFICIENT OF THE LIGHT ABSORPTION BY CHLORINE

## 1. Introduction.

The temperature coefficient of the amount of chemical change produced in a given time by light of constant intensity, is usually referred to as the temperature coefficient of the particular photo-reaction.

Such a temperature coefficient may be a function of a number of factors, the chief of which may be classified as follows:

1. Temperature coefficient of the primary process.
    (a) Temperature coefficient of the light absorption.
    (b) Temperature coefficient of the quantum efficiency of the primary activation step.
2. Temperature coefficients of the secondary processes (thermal reactions initiated by primary processes).
3. Apparent temperature coefficients derived from

certain other processes such as:

(a) The existence of internal light filters, which are either formed or destroyed throughout the reaction.

(b) Solvation.

(c) Viscosity and rates of diffusion.

It is obvious that unless a number of the above factors are ruled out, the values obtained for the resulting temperature coefficient will be of limited application.

In spite of this a great deal of work has been done on the temperature coefficient of the photo-reaction alone. This applies particularly to the earlier investigations. The data from over ninety such photo-reactions have been summarized by Dhar[1]. Fortunately, a number of the above sources of temperature coefficients are capable of being ruled out in certain cases but this is by no means general.

Despite the fact that numerous investigations of the temperature coefficients of photochemical reactions have been carried out, only in three or four cases have the temperature coefficients of the quantum yield been determined.[2-4] Such data are entirely lacking for the temperature coefficient of the quantum yield of the hydrogen-chlorine reaction. In the present work these data have been obtained for wave-lengths, 365, 405, 436, 546, and 578 $m\mu$ over a temperature range $25^{\circ}$-$100^{\circ}$.

The first step in this determination was the calculation of the temperature coefficient of the light absorption of chlorine. For this purpose two methods have been tried out, namely, a spectrophotometric method and a spectroradiometric method. Only preliminary measurements could be made with the former method due to delay in obtaining a suitable spectrograph (Section IV, 2). A detailed account of the latter method is given in Section IV, 2-12.

## 2. Preliminary Experiments using a Spectrographic Method.

In a preliminary investigation, the extinction coefficients of chlorine at room temperature were determined by a spectrographic method. The source of radiation was a pointolite lamp run from storage batteries. The radiation from this source was made parallel, passed through screen filters and chlorine, and focussed on the slit of a spectrograph. The wire screen filters of known transmission (Sect. IV, 7) were used as step-weakeners, to transmit from one hundred down to one per cent, in ten fairly evenly spaced steps.

A spectrum was first obtained with the tube empty for each step using equal exposures, the whole being taken on one plate. From the densities of the spectra at different wave-lengths, a number of characteristic curves were obtained by plotting photographic density against intensity of light.

Spectrograms of the light transmitted by the chlorine were next obtained using the same exposures as with the empty tube. The densities of these spectrograms were read by means of the densitometer described below, and the corresponding densities read from the characteristic curves previously determined. From the ratio incident to transmitted light, the extinction coefficients were computed. Ilford Process Panchromatic Plates were used, developed to unit contrast.

In order to read the densities, a densitometer was constructed from a microscope and a Moll Surface Thermopile. Constant light from a small incandescent bulb run on a storage battery, was brought to a focus, by an objective, onto a photographic plate placed on a moveable stage on the microscope. This objective was fitted on the microscope beneath the stage. The transmitted light was picked up by a second objective and thrown on to the thermopile which was fitted on the microscope in place of the draw tube. The E.M.F.'s generated were measured as in Sect. IV 10, and the densities obtained by the relationship, $\log. \frac{\text{Incident light}}{\text{Transmitted light}}.$

The microscope was fitted with a moveable stage so that different areas of the plates could be compared at will.

The results obtained by this method were in close agreement with those later obtained by the monochromator thermopile method for wave lengths 365, 405 and 436 mμ but did not agree at 579. This variance was to be expected from the low dispersion of the small Hilger Quartz Prism Spectrograph used. (E37).

It was planned to repeat these observations using a larger Littrow type of spectrograph. This instrument, unfortunately, was not available in time to make the determinations on chlorine. However, such a spectrograph has since been employed satisfactorily for the measurement of the spectral absorption of water using the above method.

These experiments indicated that the measurements on chlorine could be improved by use of the larger spectrograph.

### 3. Optical Train.

For this investigation an intense source of monochromatic light of constant intensity was required. High monochromatism can only readily be attained at the expense of intensity. However, since the photosynthesis of hydrogen chlorine has an extremely high quantum yield, it was possible to make considerable sacrifice of intensity for purity. In order to obtain maximum intensity, a very intense source of light was placed directly on the slit of a monochromator. To do this the usual slit was removed and replaced by a water cooled type.

The complete optical train is shown in Fig. 2. (A) is a quartz mercury lamp (described later) at the slit of a Bausch and Lomb Monochromator (C) is a Hilger monochromator. The prism and mirror of this monochromator were protected from stray radiation by means of a box packed with cotton wool. The light from (C) was picked up with a lens (D) of short focal length and made parallel. (E) is a set of wire screen "step-weakeners", a description of which is given later. A photographic shutter and diaphragm (F) then follow.

The absorption ($F^1$) cell was made of pyrex, with

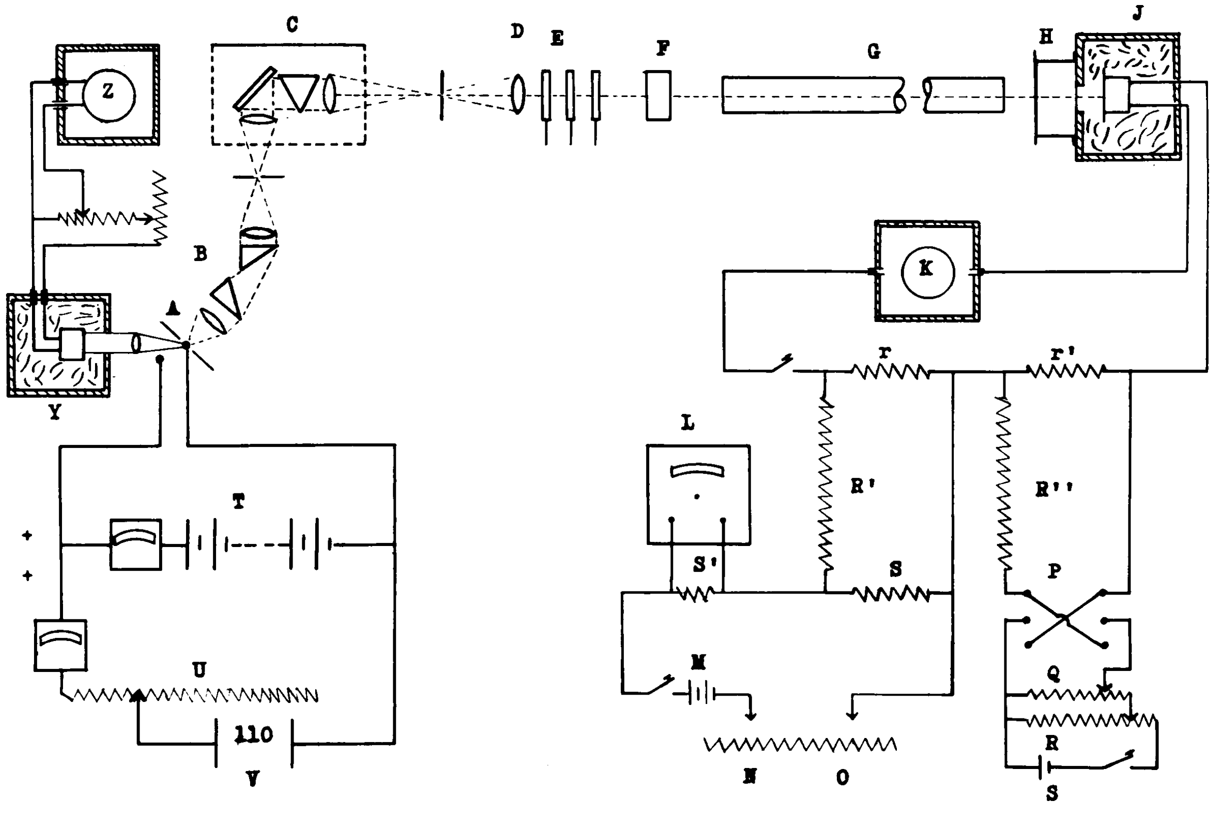

Figure II.

fused on, polished pyrex discs on the ends. The diameter was 19 m m and the length was varied, depending on the wave length used. The cell was wound with copper wire, asbestos paper, nichrome wire, and asbestos paper in the order named. The current passing through the nichrome wire was adjusted by means of a hand regulated resistance, so that the cell could be maintained at different temperatures from 25°C to 200°C.

A Moll Micro Surface Thermopile (diameter 5 m m ) was placed at (J). It was protected from stray radiation, by placing it in a box, packed with cotton wool, containing an aperture for the admission of the light from (G). Placed directly in front of the opening was a large water cell 4 cm. long. This cell, which changed its temperature very slowly, picked up any stray heat from (G).

The E.M.F. developed by the thermopile was measured by a null method. The parasitic E.M.F.'s were first neutralized and then the E.M.F. to be measured was neutralized by a known E.M.F. A complete description is given in Section IV:10.

### 4. Source of Radiation.

The usual sources of radiation used in photochemical investigations are sunlight, metal filament lamps, condensed sparks between metal electrodes, arcs between carbon, tungsten and other solids, cadmium and mercury vapour lamps.

In the present investigation, sunlight was ruled out for obvious reasons. Although filament lamps give an intense source of radiation readily made constant, their continuous nature requires an extremely narrow slit width to obtain even approximate monochromatism. Thus, they are too weak a source for convenience in measurement. The spark and arc types suffer from the disadvantages of inconstancy of source, are costly, and require complicated equipment which needs frequent attention.

The mercury arc emits a number of strong conveniently spaced lines in the visible, near and medium ultra-violet. There are many types of these arcs available, both vertical and horizontal. The vertical type is more convenient for use with the monochromator. In these lamps the cathode is always of mercury and the anode mercury or tungsten.

There are many objections to the sealed in electrode type of mercury lamp. They are slow to attain a steady state, the light intensity varying with the line voltage and ventilation. They will not stand heavy overloading. Furthermore, their initial cost is high, and freshening when the transmission has deteriorated requires considerable time and money. In those lamps using a tungsten electrode, spattering of the tungsten is an additional objection.

Forbes has had considerable success with an unsealed atmospheric pressure type of arc [5-10]. This type has also been used by Villars, [11] Vincent and Biggs, [12] and Harrington [13]. One of the simplest of these types consists of an inverted U tube, with capillaries in the lower part of the arms to restrain oscillations of the mercury. The arms are dipped in wells of mercury and the curved part of the U heated to start the arc. These lamps may be water or air cooled or both.

For the present investigation all of the above sources of light were considered and some of them

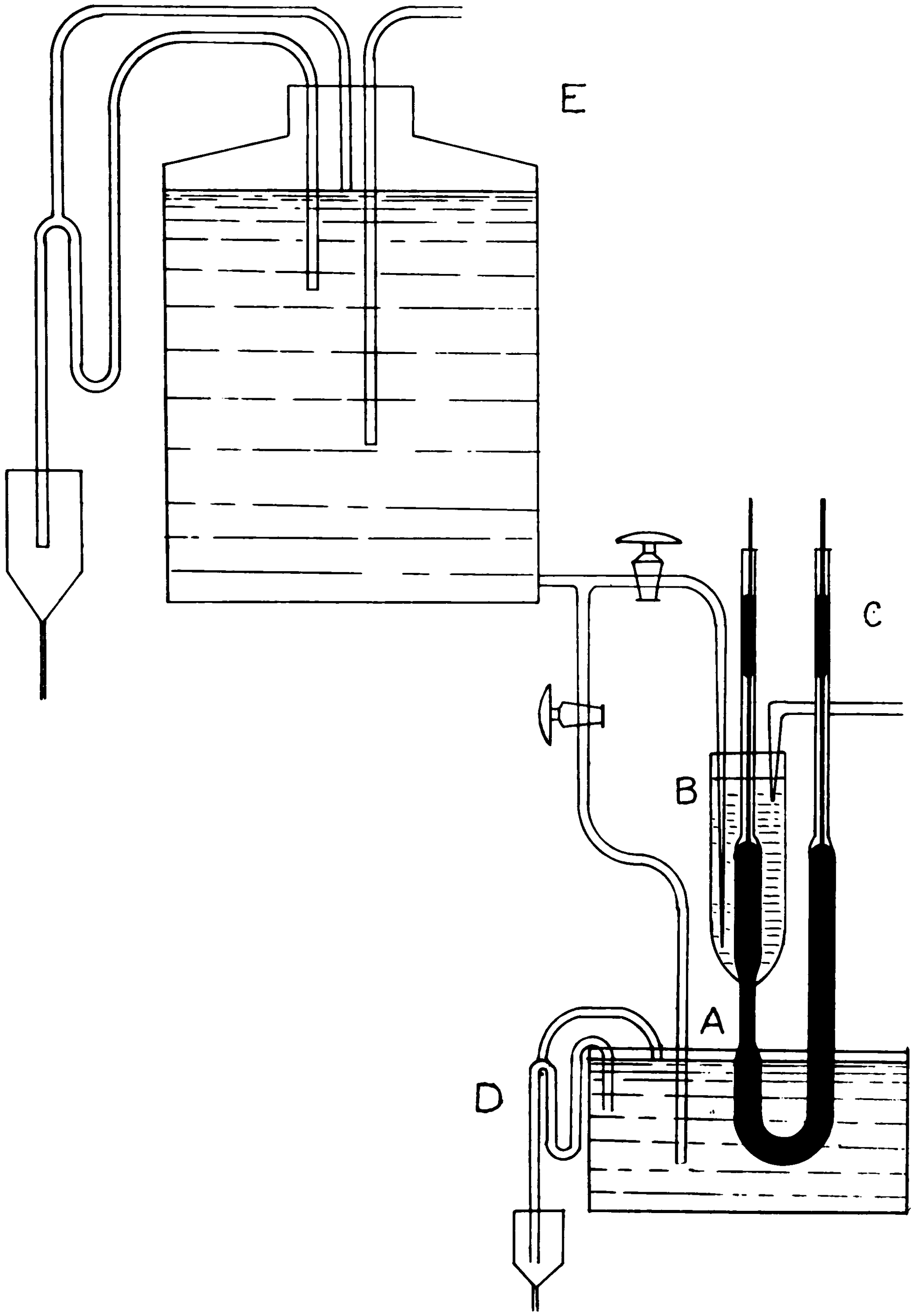

Figure III.

tried out. As a result of these experiments a new type of atmospheric pressure lamp was developed, which was simpler and proved more satisfactory than any of the others. Six different lamps were constructed and tried out before the following type was adopted. (Fig. III).

This lamp was simply a U tube made of quartz with a constricted partion at (A.), a part of the tube above (A) was surrounded by a water-jacket B. The constricted portion was 3.5 mm. inside diameter and 1 cm long, widening to 8 m m inside diameter. The capillaries were .8 m m. bore. Since Fig. III. has been drawn to scale no further dimensions will be given. Nickel wires, drawn down to fill almost the whole bore of the capillaries, made the electrical connection to the lamp. These filled the capillaries so as to restrain the oscillations in the arc and carried the current if a bubble of air broke the circuit in the capillary. Furthermore these wires could carry a heavy current without overheating. This was a decided advantage over iron wires previously used.

The lamp was filled with mercury to (C) heated with a hand torch at (A), while two amperes were passed through the circuit until the arc broke. The wider portions of the tube on either side of the constriction were to assist in cooling, thus keeping the arc within the constricted portion of the tube.

The cooling of the electrodes is self explanatory in the diagram. (D) is a constant level siphon. The constant head for the inflow being obtained by a similar, but larger device (E). In a number of other lamps of this type cooling of the upper electrode is effected by a stream of water over the electrode or the arc, or by a blast of air. Unless distilled water is used for this purpose, a deposit on the constriction of the tube is formed in time. With an air blast a similar difficulty is encountered unless the air is carefully freed of oil and dust from the blower. Moreover a stream of water on the constriction is another disadvantage when the lamp is used directly on the slit of a monochromator. The sealed on water jacket (B) overcame all these difficulties. The lamp was usually run on 4 amperes.

This lamp has the following advantages. In the first place, in common with all lamps of the unsealed constant pressure type, it is easy to construct, cheap to build; has the ability to stand overloads; is easily cleaned, filled and boiled out; rapidly attains a steady state in less than one minute and finally has a constancy of intensity when the current is kept constant.

In the second place it combines the high intensity of a constricted arc with the longer life of an ordinary arc. It is well known that the mercury arc, operating at high efficiencies, consists of an exceedingly brilliant "thread" surrounded by a comparatively dark vapour which absorbs much of its light. Thus the smaller the diameter of the arc, the greater the intensity at the sacrifice of the life of the lamp. A diameter of 3.5 mm. was chosen as a compromise between these two.

Finally the short length of arc permitted a low voltage at the terminals and hence fewer storage batteries for voltage regulation.

### 5. Intensity Control on Lamp.

In order to keep constant incident intensity on the surface of the absorption tube, the current passing through the lamp had to be kept constant. For this purpose two methods were tried out.

In the first, a hand regulated resistance was placed in series with the lamp and a large electromagnet. The electromagnet removed the small "ripples" in line voltage, the larger changes being regulated by hand. The intensity of the radiation coming directly from the lamp was determined by a second Moll Surface Thermopile. This was protected in a similar manner to the one previously mentioned. As the constancy of intensity alone was wanted, the thermopile was connected to a galvanometer (Leeds Northrup 2283a) the deflection being measured on a scale at one meter. This deflection was then maintained by altering the series resistance by hand.

In the second method, the principle of the floating battery was used. The wiring diagram is given in Fig. II. (V) is a 110 volt D.C. main whose voltage fluctuated; (U) is a hand regulated resistance, and (T) a battery of 5 six volt accumulators. It was known from a previous measurement that the potential drop across the lamp under the standard conditions of running was 30 volts for 4 amperes. When the battery was thrown in, the resistance (U) was regulated until only 0.1 amperes were being drawn from it and 3.9 amperes from the line. If, however, the line voltage decreased the amount of current taken from the battery increased, and conversely, if the line voltage increased the current from the battery decreased. Under these conditions the percentage variation in the current going through the lamp was much smaller than the percentage variation of the line voltage. The theoretical relationship is given as follows:

$$\frac{dI/I}{dV/V} = \frac{V\,r}{E\,R + V\,r}$$

where (I) is the current through the lamp, (V) the line voltage, (R) the resistance, Vr the resistance of the battery and (E) its E.M.F. Thus if V is 110,

$R = 20$, $E = 30$, and $r = 0.15$

$$\frac{dI/I}{dV/V} = \frac{16.5}{600+16.5}$$

$$= 1/27 \text{ (app.)}$$

As before the intensity of radiation was determined by the thermopile galvanometer method previously described.

By this second method the intensity could be kept constant to about 0.5 per cent. There were occasional variations greater than this which appeared to be due to a slight shift in the position of the "thread of light" in the arc.

## 6. Wave Length Control.

There are two general methods usually employed to obtain monochromatic radiation from a mercury vapour lamp. In the first method filters which transmit a narrow spectral region are used.[14 - 18] If the region is sufficiently narrow so that a given line is transmitted while the neighbouring lines or groups of lines are absorbed, pure monochromatic radiation is obtained. However, it is difficult with this method to make a complete separation of some of the mercury lines. Furthermore, as many of the filters transmit some near infra red, it is hard to obtain the true value of the energy of the hue wanted when using a thermopile method.

In the second method wave-lengths are separated by refraction dispersion. Monochromators, employing this principle,are at present relied upon as the best practical compromise between intensity and monochromatic purity.[19 - 25] In the present work, equipment was not available to construct a large monochromator so it was decided to employ two smaller ones in series.

It has been shown by Jones and Sandvik,[26] and van Cittert[27,28] that, along with monochromatic light from a single monochromator, there is a certain amount of false light or stray light, caused by scattering and reflection from various parts of the instrument. In order to obtain a minimum of false light, a second monochromator was placed in series with the first, and narrow slit widths were used.

These were set up according to the diagram in Fig. II. The slits were removed from both ends of a Bausch and Lomb Quartz Monochromator[29] and a water cooled slit placed on the collimator end, so that the lamp could be placed directly on the slit. The collimator slit of a Hilger Quartz Monochromator[30 - 33] was placed at the exit slit of the Bausch and Lomb instrument. All slits were set at 0.30 m m width and 6 m m height. The radiation transmitted by the exit slit of the Hilger Monochromator was picked up by a short focus quartz lens and rendered parallel. As both of these instruments are standard equipment and well known, a description of their optical mechanisms and dispersion constants will not be given. This data may be obtained, however, in references 30 - 33.

In some experiments instead of using a water cooled slit another method was tried out which proved successful. The lower part of the lamp in Fig. III and parts (A) and (B) were plated with a thick layer of silver. A slit 0.3 mm wide and 6 m m high was removed from part of (A). This acted as a slit for the monochromator. A circle of silver, 2 m m. in diameter, was also removed from another part of (A), and acted as a point source to focus the light from the lamp on to the thermopile (Y) Fig. II.

The light emitted by the monochromator was examined visually and by means of a spectrograph and found to be of a high degree of purity. The lines 578, 546, 436, 405, 365 m$\mu$, were selected as being sufficiently intense for the work. It is customary in general photochemical work to express the wave-lengths of these lines as above, although only two of them 546 and 436 are single lines. The true wave-lengths of these lines obtained from the usual mercury arc are given in Table I. The above nomenclature, however, is retained throughout the text for the sake of brevity.

### 7. Variation of Incident Intensity by Wire Screen Filters.

It was necessary to be able to vary the incident intensity by known amounts. A number of methods (for summary see 34, 35) are commonly employed for this purpose, such as the use of the inverse square law, neutral wedges, sector wheels, Nicol Prisms, variation of area of source, solutions of dyes obeying Beer's Law, punched plates, and wire screens. The inverse square law method is not practical with a spectrograph. A sector wheel or Nicol Prisms were not available for the present work. Solutions of dyes and neutral filters are selective and have to be calibrated for different wave-lengths.

Wire screens have a number of advantages over the above methods. They are readily calibrated, using either white or monochromatic light, by means of a thermopile. Repeated comparisons between calibration curves obtained with filters and with screens have shown excellent agreement, except that the screen curves were more regular. This is probably due to the fact that it is easier to make a uniform screen than a uniform filter. It is also easier to keep the former free from grease and scratches. For these reasons it was decided, in the present investigation, to use wire screens for varying the incident intensity of the light.

Screen filters were first tried by Ham, Fehr and Bitner [36]. Harrison [37] made a thorough study of their use and discussed the question of elimination of errors.

Screen Filter Rocking Apparatus.

Harrison found that the best procedure in using screen filters was to keep them moving in uniform circular motion of about 1 cm. amplitude, without rotation. Employing these principles, an apparatus was constructed for moving the screen filters. A picture of this instrument is shown in Fig. IV. The dimensions are given in the diagrams in Fig. V.

(A) is a shaft carrying three eccentric collars with bands (B). Fastened to the bands are three arms (C) with slots (D). A second shaft (E) passes through the slots. Connected to the ends of arms (C)

**Figure IV.**

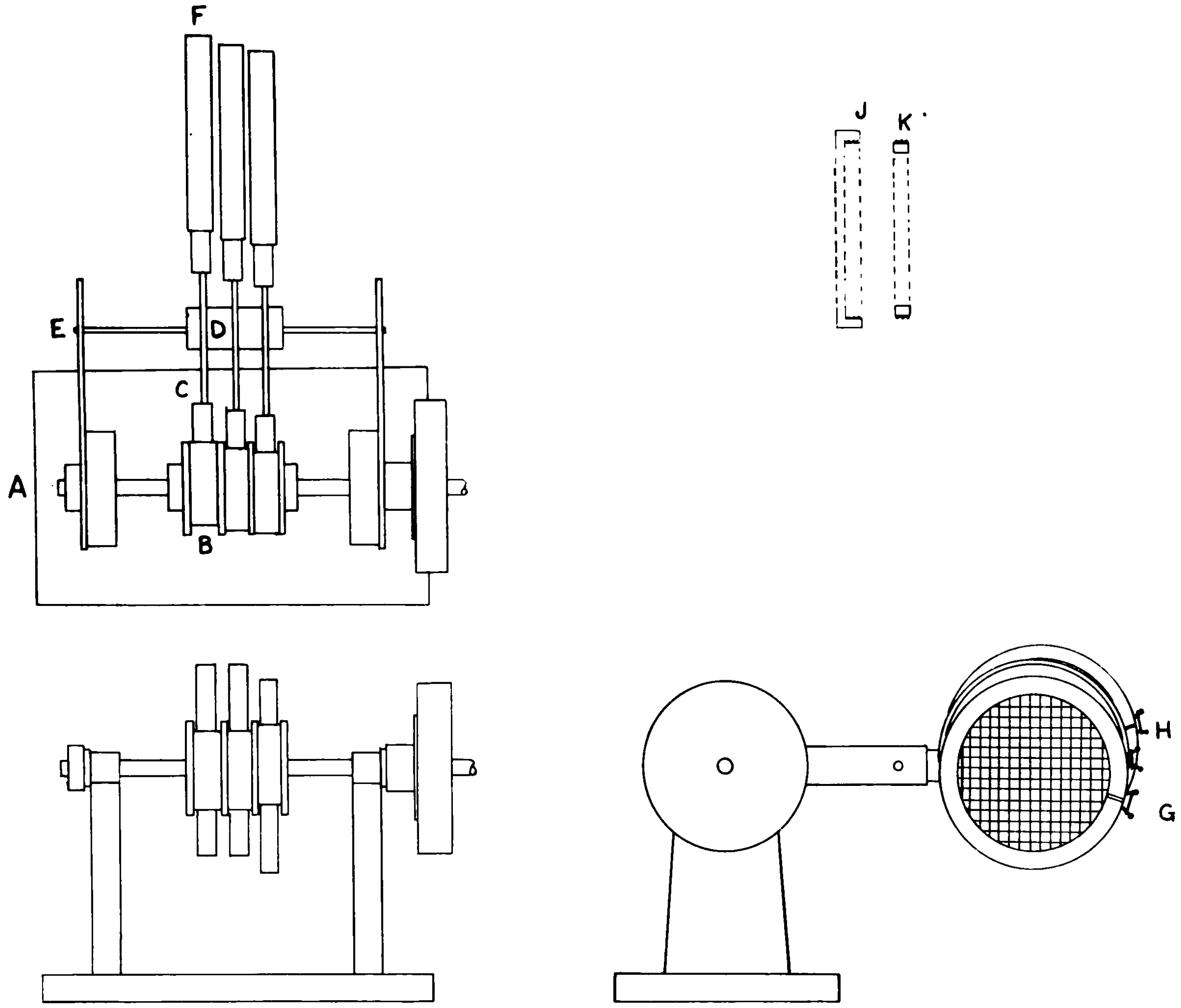

Figure V.

are three bands (F), which are cut at (G). A pair of pegs at (H) on each enables the bands to be drawn so as to hold the screen holder (J). The shaft was rotated at 120 revolutions per minute, moving the screens with uniform circular motion of about 1 cm amplitude without rotating them. The whole apparatus was made of brass with the exception of the base (L). The wire screens are held in the screen holders (J) by screwing down the inner ring (K). Brass wire mesh rather than copper was selected for the screens as a much more complete range of sizes could be obtained.

The two methods which had been previously used to blacken the screens, namely smoking or heating in a flame proved unsatisfactory. Both gave non-uniform screens. It was found, however, that, if the screens were left for two days in hydrogen sulphide water and then exposed to the air to dry, uniform blackening was obtained with no damage to the screen. The screens were placed in the holders singly or in pairs. When placed in pairs they were rotated until the resulting moiré pattern had the finest structure. A number of filter holders were built so that the double screens need not be removed. The screens were in all cases treated as optical parts.

With such a large range of screens to choose from, the incident intensity could be weakened in evenly spaced steps over a thousandfold range.

## 8. Measurement of the Chlorine Pressure.

The simplest manometer to use with chlorine is one employing concentrated sulphuric acid. This type has been used by a number of authors,[38 - 41] but, as Melander[42] has shown that sulphuric acid affects the thermal union of hydrogen and chlorine, there is a possibility of some complex being formed with the activated chlorine in the absorption tube. It was therefore decided, in the present investigation, to use some form of glass manometer.

### Glass Diaphragm Manometer.

A survey of the literature revealed a number of glass enclosed systems, depending on the flexibility of glass, for the indirect measurement of pressure[43 - 57]. That used by Wright[57] possessed a number of advantages, as follows: ease of construction, operation and cleaning; ruggedness, readily thermostated; low temperature coefficient; pressure changes may be followed continuously; and finally freedom from errors, due to accidental movement of the mirrors, scales etc., that occur with some optical methods.

A diagram of one of the glass diaphragm mano-

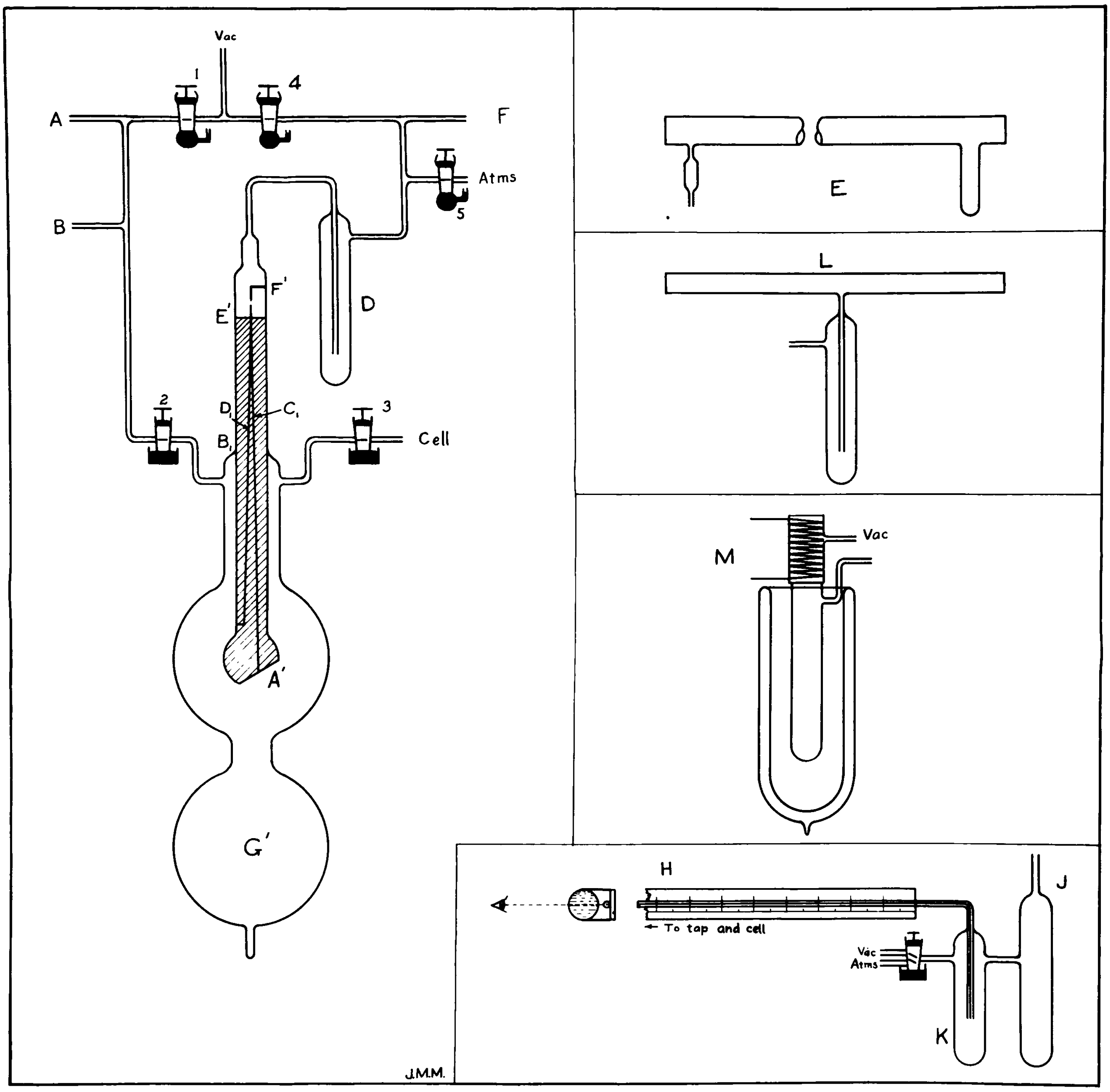
Vac
1
4
A
F
Atms
5
B
D
F'
E'
D₁
C₁
2
3
B₁
Cell
A'
G'
J.M.M.
E
L
M
Vac
H
J
← To tap and cell
Vac
Atms
K

Figure VI.

meters used in given in Fig. VI (C). (A') is a thin diaphragm blown at the end of a long tube which is sealed into a larger tube at (B'). The larger tube was in communication with the chlorine supply through (A), and with the absorption tube and reaction cell E. The inner tube with pointer,was connected through trap (D), with a mercury manometer (F). This manometer had an etched mirror scale readable to 0.1 m m. Attached to the diaphragm of the glass manometer (A') was a long pointer (C',D') with a blackened tip. This pointer was bifurcated at the fixed end in order to obtain greater magnification (see diagram). The vibration of the pointer was damped by filling it to (E') with oil, the trap (D) being used to protect the manometer etc. from the oil. (F') is a fixed index.

The movement of the pointer relative to the fixed index, when unequal pressures were applied to the two sides of the diaphragm, was greatly magnified by the following optical arrangement. The tips of the pointer and index were illuminated by a strong lamp with condensing lens. Their images were thrown onto a mirror 2.5 meters away and reflected back onto a scale conveniently situated with regard to the manometer (F) and taps (4) and (5). In this way a great magnification of the movement was obtained.

The glass diaphragm manometer was used as a null instrument, the unknown pressure in (C') being balanced against a known pressure determined by (F). It was found that for a considerable range in the neighborhood of the null point, the deviation of the position of the pointer relative to the index was proportional to the difference in pressure on opposite sides of the diaphragm. This greatly simplified the operation of the apparatus as only an approximate pressure balance was necessary, a correction later being applied to the pressure read on the mercury manometer (F). The difference in pressure for a 1 m m. displacement on the scale is a measure of the sensitivity of the instrument and following the terminology used by Wright was called the displacement constant. For one of the manometers used, it was found to be 0.42 m m $(H_g)$ per m m. displacement of the pointer on the scale. The displacement was read to 0.5 m m.

thus giving the instrument a sensitivity of 0.2 m m.

The diaphragm manometer was employed as follows for determining the pressure of the chlorine in (E). Before filling, both sides of the diaphragm as well as (E) were evacuated simultaneously. Chlorine was then let in slowly from (A) and at the same time air was let in by tap (5) in sufficient amounts to keep the pointer near the null point. When very near the required pressure was obtained, the chlorine was shut off and the air continued until the mercury manometer (F) read the pressure required. The chlorine was then let in slowly until the pointer was brought back, approximately to the null point. The chlorine supply was then shut off, and the pointer displacement, the manometer (F), the temperature and the barometer read.

## 9. Measurement of the Chlorine Concentration.

In order to determine the molecular extinction coefficients of chlorine, it is necessary to know the concentration of the chlorine in moles per litre contained in the absorption cell.

The absorption cells were made of pyrex (20 m m in diameter and varying lengths) with fused on, plane parallel, polished pyrex discs on the ends. The absorption tubes were connected to the glass diaphragm manometer (B') through a liquid air trap and tap. (These replaced (D') and the reaction cell in Fig.I.)

The volume of the diaphragm manometer from tap to tap had been previously determined by weighing the volume of water it contained. The volume of the absorption tube was determined by observing the change in pressure when hydrogen of known pressure in (B') was let into the evacuated absorption cell.

In order to fill the cell with a given mass of chlorine, (B') was kept at 0°C by surrounding it with a large Dewar Flask containing ice and water. The pressure was read, the flask removed, the tap opened and the chlorine condensed into the cell by means of liquid air. From the vapour densities found by Pier[62] the mass of chlorine originally present in the known volume (B') was calculated and from this the concentration in the absorption cell in moles per liter.

## 10. Measurement of Light Intensity and Absorption.

In almost every investigation in photochemistry where the light intensity has been measured by means of a thermopile method, the direct deflection of a galvanometer with or without shunts has been used as a measure of the E.M.F. generated. In order to obtain the intensity values in absolute units, a thermopile, which has been compared with a standard lamp or Leslie Cube is usually employed.

There are a number of objections to using the direct deflection of a galvanometer for the above work, among which are the following; non linearity of scale, temperature changes in the earth's magnetic field, leveling, zero creep, etc. The magnitude of any of the above corrections varies with the type of galvanometer used. (Suspended coil or magnet types). Another serious objection enters in, when light intensities differing greatly in magnitude are used. For such work shunts have to be employed which change certain characteristics of the instruments and necessitate a different calibration for each shunt. It is very difficult to rule out most of the above objections even with frequent calibration.

As the constants of a thermopile remain comparatively fixed over a long time, it was decided to measure the E.M.F. directly. A Leeds and Northrup, type K, Potentiometer was tried in conjunction with one of their type H.S. galvanometers. However, this arrangement was found unsatisfactory for the evaluation of small E.M.F.'s of the order of 10 - .1 microvolts. Part of the trouble was traced to E.M.F.'s generated in the stud contacts and dials.

It was therefore decided to try another method of balancing the E.M.F., using a circuit with the minimum number of sources of parasitic E.M.F.'s. The method finally adopted was that shown in Fig. II.

The primary or low potential circuit consists of thermopile galvanometer (K), close-pin Key (J) and resistance (r)(r'). In this circuit there were no moving contacts. The secondary circuit (r', R",
P,Q,R,S) was used to neutralize any small constant E.M.F.'s which often exist when no radiation is

falling on the thermopile. These are often due to differences in temperature of parts of the thermopile.

The function of the other secondary circuit ( r, R', S, S', L, M and O) was to neutralize the E.M.F. developed when radiation was falling on the pile. R' and R" are resistance boxes, (r) a resistance (0.1000 ± 0.002) ohms, (r') approximately 0.1 ohms. The shunt S is 1.000 ± 0.002 ohms, (L) is an ammeter reading from 0.01 amperes to 1.5 amperes. (N,O,Q,R) are four sliding resistances, a coarse and fine one in each pair. (M) and (S) are accumulators and (P) a reversing switch.

The method of determining an E.M.F. was as follows. The two secondary circuits being open, the key in the primary was closed, any deflection being shown on (K). The deflected beam from the mirror of (K) was returned to zero by moving the sliding contact of the coarser rheostat (potential divider), the final adjustment being made by (Q). The above parasitic E.M.F. having been neutralized, the radiation was allowed to fall on the thermopile and the deflection obtained. By adjusting the current flowing through (S), by means of (N) and (O), a varying potential drop across (S) (R) and (r), depending on the resistance of each, was obtained.

The drop across (r) is given by the equation $I\,S = \frac{r}{R+r}$, where I is equal to the current recorded. With $S = 0.1$, $r = 0.1$, $R' = 10{,}000$ ohms respectively the E.M.F. corresponding to 1 ampere read on the ammeter is one microvolt ± 0.005. The galvanometer determined the sensitivity of the measurement. For this work a carefully shielded (heat and currents) Leeds and Northrup, type HS, d'Arsonval Galvanometer was used, with the proper damping resistance in series. The scale was placed at 4 metres. The E.M.F. could be estimated to 0.005 microvolts, by reading the scale to 0.1 m m.

The diameter of the Beam of light passing through the absorption tube, was reduced to 6 m m. by an iris diaphragm on the shutter (F). This beam of light just covered the surface of the thermopile (reflector not used).

The ratio of the E.M.F.'s, $E_0$ and E, with cell evacuated and filled with chlorine respectively was assumed equal to the ratio of the incident and transmitted intensities $I_0$ and I. From the value of the extinction ($\log \frac{I_o}{I}$), the extinction coefficients were calculated for different depths and concentrations of chlorine, using the expression:

$$\log \frac{I_o}{I} = e_m\, c\, d = e\, d$$

Where $e_m$ is the molecular extinction coefficient, C the concentration in moles / litre, d the depth in cm, and $e$ the extinction coefficient of the gas at N.T.P.

The results are given in tables (I - V), a sample calculation being given on the following page.

## II. CALCULATION OF RESULTS.

### Sample Calculation of Extinction Coefficients.

| | |
|---|---|
| Wave-length | 546 mμ |
| Depth of cell (d) | 274.5 cm |
| Temperature | 25.1 °C |
| Vol. diaphragm manometer from weight of water it contained | 1017.1 cc |
| Pressure of $H_2$ (p) | 762.4 mm |
| Pressure of $H_2$ after expansion into cell (p') | 400.0 mm |
| Vol. manometer + cell (v') $\left(\frac{1017.1 \times 762.4}{400.0}\right) =$ | 1937.0 cc |
| Volume of cell | 921.1 cc |
| Pressure of $Cl_2$ in manometer | 761.5 mm |
| Weight of $Cl_2$ in manometer $1.017 \times 1.293 \times 2.490 \times \frac{761.5}{760.0} =$ | 3.281 g |
| Concentration in moles / liter $\left(\frac{3.281}{0.9211 \times 70.92}\right) =$ | 0.5022 |
| Ratio of light intensities $\frac{E}{E_0} = \frac{I}{I_0} =$ | 0.9424 |
| Molecular extinction coefficient. $e_m = \frac{1}{c.d.} \cdot \log \frac{I_0}{I} = \left(\frac{0.02577}{0.05022 \times 274.5}\right) =$ | 0.00187 |
| Extinction Coefficient. $e = 0.04538\ e_m$ Since $\frac{1.293 \times 2.490}{70.92} =$ | 0.04538 |
| $= 0.0454 \times 0.00187 =$ | 0.000085 |

## 12. DISCUSSION

### METHODS

Unfortunately it was not possible to compare the experimental results of the two methods, namely, the photographic (Sect lV, 2) and the thermopile (Sect lV, 3-12), as those obtained from the former were only of a preliminary nature. However, from the experience gained, it is possible in a general way to compare the advantages and disadvantages of the methods themselves. From the point of view of standard equipment required, they are about the same. With the equipment on hand the photographic is easier to set up; easier to keep in adjustment; light source can be more readily kept constant; the absorption for all wave-lengths can be obtained at one exposure and the simultaneous reading of two thermopiles is not necessary. The chief advantage, however, and a very important one is the fact that a very large range of wave-lengths can be obtained compared to the few which are possible with the mercury arc thermopile method. Naturally the type of spectrograph used is the key to the utility of the method.

The precision of this method is limited by the use of photographic plates. In the general practice of photographic photometry the deviation measure (Goodwin)[59] is about 5 percent, although, it was found possible to keep it under one percent, by following the proper precautions [60,61]. However, absolute errors (1 percent) are involved from the use of the photographic plate. The relative error $\frac{d\,E}{E}$ may be decreased by increasing the extinction (E).

One of the chief objections to using the thermopile method, is the difficulty in keeping the intensity of the mercury arc constant, even with constant current. However, this may be overcome by the simultaneous reading of the thermopiles. Under these conditions the deviation measure was found to be 1/1000, with five to eight separate readings.

The great disadvantage of this method was that only few measurements could be made in the part of the spectrum in which we were interested.

However, this is an advantage as well, as the greater distance between the lines gives greater monochromatism. Furthermore, when the absolute value of the absorption is required as in this investigation, a thermopile method must be employed. This method is also convenient in that it gives the results immediately..

## RESULTS

In table I the molecular extinction coefficients obtained in this investigation at room temperature are compared with those of Halban and Siedentopf[22] also at room temperature. The exact values of the wave-lengths used are also included in this table. Tables 11, 111, 1V, V, and V1, give the temperature coefficients of the extinction coefficients obtained at temperatures of 25, 35, 50, 75, 100°C. A summary of these temperature coefficients is presented in graphic form in Fig. V111.

The only data with which to check these results are those of Halban and Siedentopf. They, however, worked only at room temperature. At wave-lengths 366, 405, 436 mμ the agreement of their results with those obtained in the present work is quite good, but, at 546, 578 there is considerable disagreement. However, when it is remembered that the absorption at 546 for 3 meters at N.T.P. is only of the order of 0.0002 per cent, such disagreement might be expected. Kuhn[62] made a study of the change in the intensity of absorption of certain bands with temperature. However, as he has pointed out in a "note added in proof" in a recent paper of Eliots'[63] that his previous results are in error, it is useless to discuss them here.

The data on extinction coefficients at higher temperatures would carry more weight if they had been obtained at more temperatures and if they had been checked by the photographic method. This check would be of value at the higher temperatures to eliminate all doubts as to the possible errors due to heating effects in the thermopile method. However, the policy followed in this study as a whole was to obtain information on a number of points of interest rather than to confine our attention to a very thorough investigation of any one phase of the problem.

## TABLE I.

### Comparison of Molecular Extinction Coefficients at Room Temperature

| Wave Lengths mu | | Relative Intensity | $e_m$ Halban Siedentopf | $e_m$ Sawyer |
|---|---|---|---|---|
| | I C.T. | | | |
| 366 | 365.015 | 10 | 27.17 | 27.25 |
| | 365.483 | 7 | | |
| | 366.287 | 4 | | |
| | 366.327 | 6 | | |
| 405 | 404.656 | 10 | 3.99 | 4.030 |
| | 407.78 | 7 | | |
| 436 | 435.834 | 10 | 1.636 | 1.652 |
| 546 | 546.073 | 10 | 0.00172 | 0.00187 |
| 578 | 576.960 | 10 | 0.0003 | 0.00021 |
| | 579.066 | 10 | | |

---

1. C. T. 5, 299 (1929).

# TABLE II.

## Extinction Coefficients at $24.6^{o}$

$$e_m cd = \log 1^{o}/I$$

| $\lambda$ mμ | c | d | $1/1_o$ | $e_m$ | e |
|---|---|---|---|---|---|
| 366 | 0.05022 | 0.791 | 0.0828 | 27.25 | 1.23 |
| 405 | 0.05022 | 0.791 | 0.6916 | 4.03 | 0.182 |
| 436 | 0.05022 | 0.791 | 0.8598 | 1.652 | 0.0749 |
| 546 | 0.05022 | 274.5 | 0.9423 | 0.00187 | 0.0000849 |
| 578 | 0.05022 | 274.5 | 0.9933 | 0.00021 | 0.0000095 |

## TABLE III.

### Extinction Coefficients at 34.7°

$e_m cd = \log I^0/I$

| $\lambda$ mμ | c | d | $I/I_0$ | $e_m$ | e |
|---|---|---|---|---|---|
| 366 | 0.05022 | 0.791 | 0.0740 | 28.47 | 1.292 |
| 405 | 0.05022 | 0.791 | 0.6795 | 4.22 | 0.192 |
| 436 | 0.05022 | 0.791 | 0.8486 | 1.795 | 0.0814 |
| 546 | 0.05022 | 274.5 | 0.9090 | 0.00300 | 0.000136 |
| 578 | 0.05022 | 274.5 | 0.9878 | 0.00038 | 0.000017 |

# TABLE IV.

## Extinction Coefficients at 49.4°

$$e_m cd = \log I^{\circ}/I$$

| $\lambda$<br>mμ | c | d | $I/I_0$ | $e_m$ | e |
|---|---|---|---|---|---|
| 366 | 0.05022 | 0.791 | -0.0617 | 30.46 | 1.382 |
| 405 | 0.05022 | 0.791 | 0.6615 | 4.52 | 0.205 |
| 436 | 0.05022 | 0.791 | 0.8315 | 2.016 | 0.0915 |
| 546 | 0.05022 | 274.5 | 0.8356 | 0.0057 | 0.000257 |
| 578 | 0.05022 | 274.5 | 0.9731 | 0.00086 | 0.000039 |

## TABLE V.

### Extinction Coefficients at 75.2°

$$-e_m c d = \log I^0/I$$

| $\lambda$<br>m$\mu$ | c | d | $I/I_0$ | $e_m$ | e |
|---|---|---|---|---|---|
| 366 | 0.05022 | 0.791 | 0.0461 | 33.63 | 1.526 |
| 405 | 0.05022 | 0.791 | 0.6362 | 4.94 | 0.224 |
| 436 | 0.05022 | 0.791 | 0.8022 | 2.408 | 0.1093 |
| 546 | 0.05022 | 274.5 | 0.6002 | 0.0161 | 0.0073 |
| 578 | 0.05022 | 274.5 | 0.9315 | 0.0022 | 0.00010 |

# TABLE VI.

## Extinction Coefficients at 99.9°

$e_m cd = \log I^o/I$

| λ<br>mμ | c | d | $I/I_o$ | $e_m$ | e |
|---|---|---|---|---|---|
| 366 | 0.05022 | 0.791 | 0.0176 | 44.15 | 2.003 |
| 405 | 0.05022 | 0.791 | 0.6088 | 5.42 | 0.2460 |
| 436 | 0.05022 | 0.791 | 0.7751 | 2.784 | 0.1263 |
| 546 | 0.05022 | 274.5 | 0.0706 | 0.083 | 0.0038 |
| 578 | 0.05022 | 274.5 | 0.7206 | 0.010 | 0.00047 |

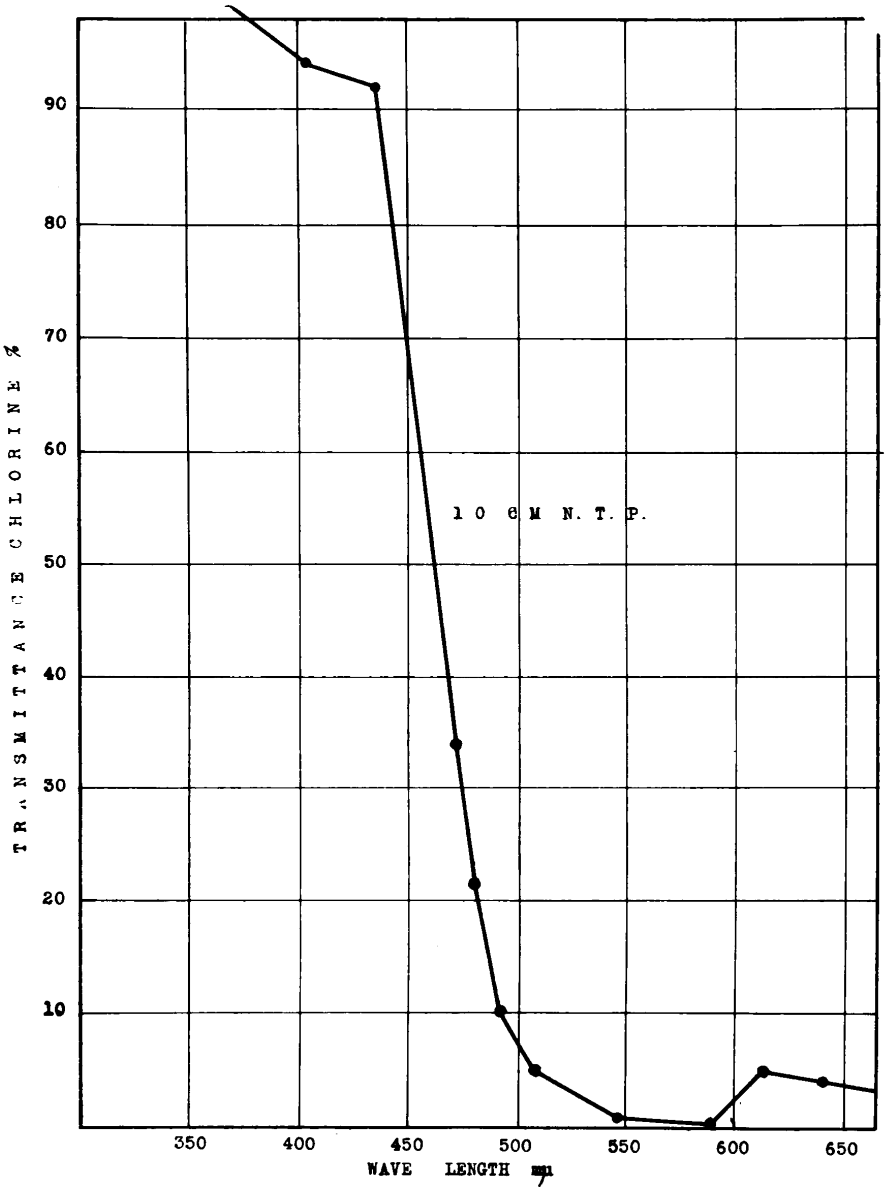
90
80
70
60
50
40
30
20
10
TRANSMITTANCE CHLORINE %
1 0 CM N. T. P.
350
400
450
500
550
600
650
WAVE LENGTH mμ

Figure VII.

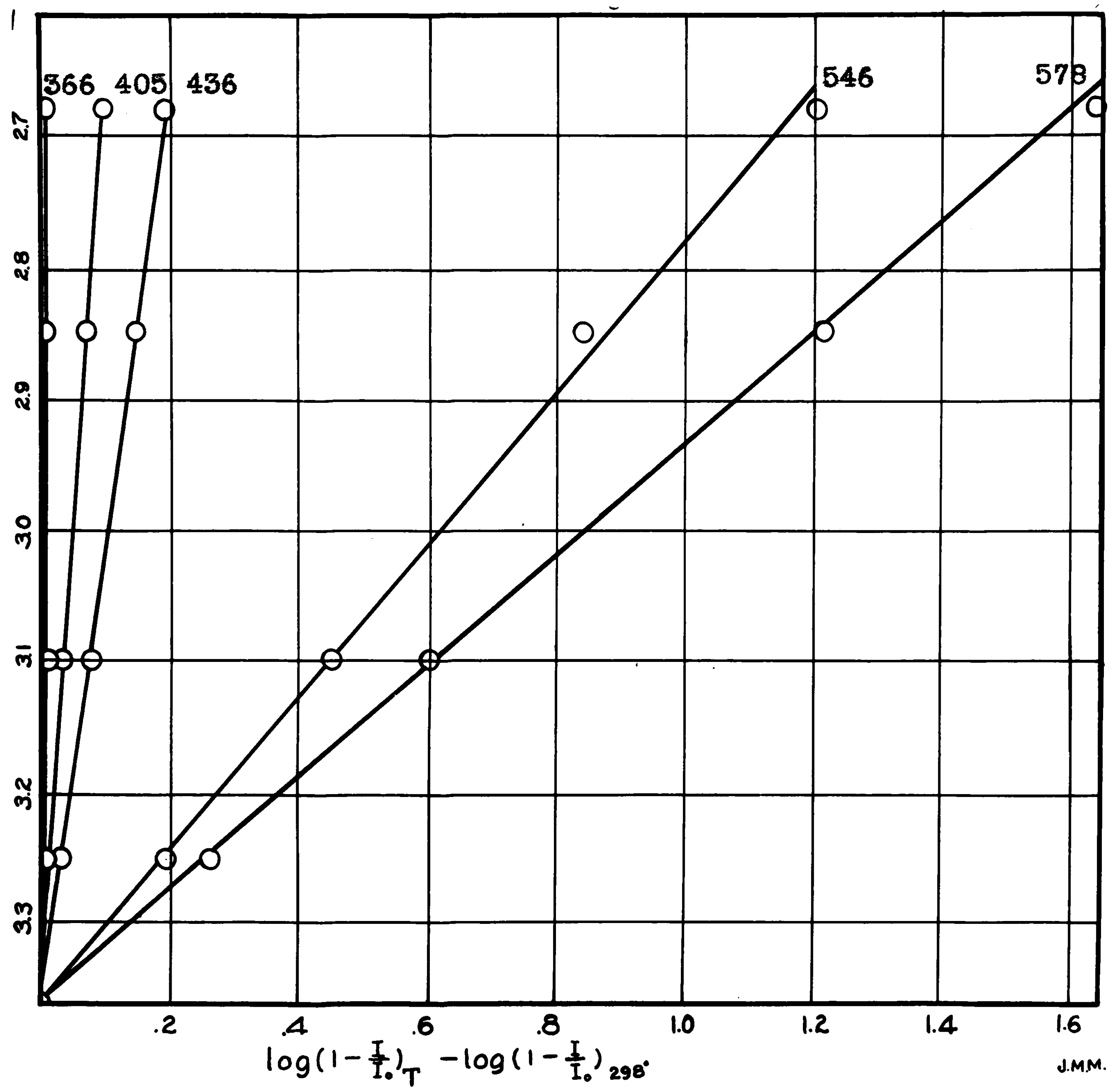
366
405
436
546
578
2.7
2.8
2.9
3.0
3.1
3.2
3.3
.2
.4
.6
.8
1.0
1.2
1.4
1.6
$\log(1-\frac{I}{I_0})_T - \log(1-\frac{I}{I_0})_{298°}$
J.M.M.

Figure VIII.

## SECTION IV

## References

1. Dhar, The Chemical Action of Light, Blackie and Son Limited, First edition 1931.
2. Kuhn, Compt. rend., 178, 708 (1924).
3. Macdonald, J. Chem. Soc., 1 (1928).
4. Ramsperger, J. A. C. S., 50, 123 (1928)
5. Harrison and Forbes, J.O.S.A., 10, 1 (1925)
6. Forbes and Harrison, J.O.S.A., 11, 99 (1925)
7. Forbes and Harrison, J.A.C.S., 47, 2449 (1925)
8. Forbes and Leighton, J.Phys. Chem., 30, 1628 (1926)
9. Leighton and Forbes, J.A.C.S., 51, 3549 (1929)
10. Leighton and Forbes, J.A.C.S., 52, 3139 (1930)
11. Villars, J.A.C.S., 49, 326 (1927)
12. Vincent and Biggs, J. Sc. Inst., 1, 242 (1924)
13. Harrington, J.A.C.S., 7, 689 (1923)
14. Winther, I.C.T., 7, 160 (1930)
15. Jones, J.O.S.A., 16, 259 (1928)
16. Dahm, J.O.S.A., 15, 266 (1927)
17. Gibson, Sc. paper Bur. Std.,No 440 (1922)
18. Stockburger and Burns, Pub. M.I.T., 65, 1263 (1929)
19. Fabry, Rev. d' Optique, 1, 413, 445 (1927)
20. Athanasau, ibid., 4, 65 (1925)

21. Beatty, J. Sc. Instr., 1, 33 (1923)

22. Halban and Siedentopf, Z. physik, Chem., 100, 212 (1922)

23. Kurtz, J.O.S.A., 13, 495, 1927 (1926)

24. Liess, Ann. Physik., 31, 488 (1925)

25. Villars, J.A.C.S., 12, 401 (1926)

26. Jones and Sandvik, J.O.S.A., 12, 401 (1926)

27. Van Cittert, Rev. d' Optique, 2, 57 (1923)

28. Van Cittert, ibid., 5, 393 (1926)

29. Bausch and Lomb, Rochester Catalogue

30. Hilger, London catalogue

31. Reeve, J. Phys. Chem., 29, 39 (1925)

32. Franklin, Maddison and Reeve, ibid., 29, 713 (1925)

33. Ridyard and Style, ibid, 32, 861 (1928)

34. Harrison, J.O.S.A., 19, 267 (1929)

35. Gibson, J.O.S.A., 10, 127 (1925)

36. Ham, Fehr and Bitner, J. Franklin Inst. 178, 299 (1924)

37. Harrison, J.O.S.A., 18, 492 (1929)

38. Rollefson and Lindquist, J.A.C.S., 52, 2793 (1930)

39. Heymer, Diss. Göttingen (1927)

40. Coehn and Heymer, Ber., 59, 1794 (1926)

41. Trifonov, Z. physik, Chem., B, 6, 118 (1929)

42. Melander, Arkiv. Kem. Min. Geol., 5, 1 (1914)

43. Baume and Robert, Compt. Rend., 168, 1199 (1919)

44. Bodenstein and Katayama, Z. physik. Chem., 69, 26 (1909)

45. Bodenstein, Z. Elektrochem., 15, 244 (1909)

46. Daniels, J.A.C.S., 50, 1115 (1928)

47. Daniels and Bright, J.A.C.S., 42, 1131 (1920)

48. Gibson, Proc. Roy. Soc. Edinburgh, 33, 1 (1912)

49. Jackson, J. Chem. Soc., 99, 1066 (1911)

50. Johnson, Z. physik. Chem., 61, 457 (1907)

51. Karrer, Johnston and Wolf, J. Ind. Eng. Chem., 14, 1015 (1922)

52. Ladenburg and Lehman, Ber., 8, 20 (1906)

53. Norrish, J. Chem. Soc., 127, 2316 (1925)

54. Preuner and Brockmöller, Z. physik. Chem, 81, 129 (1912)

55. Smith and Taylor, J.A.C.S., 46, 1393 (1924)

56. Warburg and Leithausen, Ann. Phys., 24, 25 (1907)

57. Wright, Diss., McGill 1931

58. Pier, Z. physik, Chem, 62, 385 (1908)

59. Goodwin, Precision of Measurements and Graphical methods, Second edition, 1919 McGraw-Hill Book Comp, Inc.

60. Dobson, Griffith, Harrison, Photographic Photometry, First edition, Oxford Clarendon Press 1926

61. Halban and Eisenbrand, Proc. Roy. Soc. A, <u>116</u>, 153 (1927)

62. Kuhn, Z. physik., <u>39</u>, 77 (1927)

63. Eliot, Proc. Roy. Soc., A, <u>127</u>, 638, 1930

## SECTION V.

### 1. The Effect of Light Intensity

(Using the Bunsen Roscoe Technique)

At the time when the above study was commenced the greatest range over which the intensity variation of the incident light had been tried was 1;64 (Kornfeld and Müller[1]). They found direct proportionality between rate of reaction and intensity. This was in accord with the early work of Draper and Bunsen, and Roscoe, which was confirmed later by Chapman[2] (1:6) and Marshall[3] (1;20).

However, Baly and Barker[4] found that the combination of Chlorine and hydrogen proceeded at a rate proportional to a power of the intensity greater than unity. This was of interest if true, as only one other case of a photo-reaction proceeding at a rate proportional to a power of the intensity greater than unity, had been reported[5].

Just as the experimental work described in this section had been completed, Allmand and Beesley[6] published data on the above work, over a intensity range 1:440. They found that at 436 mμ the rate was proportional to the intensity.

The results obtained in the present investigation will, however, be described in the following pages because the experimental technique was carried out in such a manner as to eliminate some of the weak points in Allmand's procedure.

## 2. DESCRIPTION OF APPARATUS

### Optical Train

A 500 Watt tungsten filament lamp was used as a light source. A two liter pyrex R. B. flash filled with 1 per cent copper sulphate solution was used to remove the infra-red and to act as a condensing lens. The light was then picked up by a lens and focussed on a 2 mm. aperture in an aluminium plate. The emergent light was made parallel by a second lens and a beam 15 mm. in diameter, passed successively through a set of screen filters, photographic shutter, Wratten 49 filter and the reaction cell. A second plate and lens system similar to the one described was placed on the opposite side of the lamp. A 2 cm portion of the parallel beam was then directed on to the thermopile as described in Section IV, 5.

### Regulation and Control of Incident Intensity.

The intensity was maintained constant by means of a hand regulated resistance as described in Section IV, 5, any variation being shown by means of the thermopile and galvanometer system. By working after midnight the intensity could be kept constant to just under one per cent .

The intensity incident on the cell was varied by means of the screen filters (Section IV, 7). Screen filters, sets of 1, 0.5, 0.2, 0.1 per cent transmission respectively, were used to vary the intensity over a range of 1-500.

In order to obtain precise results when using the capillary indicating tube, it is necessary to work with velocities of approximately the same rate. It is, therefore, necessary to increase the area irradiated simultaneously with the reduction in intensity. By using an area ratio of 1:200 and a velocity ration of 1:2.5, a five hundredfold range of intensity change may be obtained. The area of incident beam was reduced by a large or small diaphragm with apertures of 1.015 mm and 14.41 mm in diameter. The diaphragms were carefully machined and their diameters accurately determined by measuring the diameter of the blackened circles obtained when pieces of photographic printing out paper were exposed behind and in contact with the diaphragms. The diameter of the circle was obtained by using a microscope with micrometer eyepiece.

A Wratten[49] filter in combination with copper sulphate transmit a band 380 - 500 mμ (maximum 460)[7].

## Reaction Cell

The reaction cell was a pyrex tube 1.9 X 20.05 cm with fused on, polished, plane paralled pyrex plates. Two holes 20 cm in diameter were drilled in opposite sides of a wooden bucket and the cell sealed in so that only 2 mm of the ends projected. The bucket was fitted up as a thermostat and regulated to 0.01°C. The beam was sent through the reaction cell off center, so that when the widest aperture was used, a volume of water could remain in the bottom of the cell without obstructing the beam. The smallest possible diameter of tube was used so as to assist the thermostat in handling the heating from the Budde effect and heat of reaction.

## Capillary Indicating Tube

Connected to the reaction cell was a capillary indicating tube shown in Fig. VI. Water which had been introduced into (J) and purified by freezing and melting in vacuo, was distilled into (K). The capillary was 2 mm in diameter and 1 meter long and had a scale attached to it. The scale was calibrated by weighing the mercury contained in 10 cm lengths and corrections were applied to the readings.

## Precautions Against False Light.

The false light from the source was screened so that the room was comparatively dark. All parts of the apparatus containing hydrogen and chlorine were covered with some combination of black paint, electric tape, velvet or paper taken from the spool of a photographic film, depending on the size and position of the part concerned. The capillary indicator was protected from active light by enclosing with a box with an opening for reading the capillary and scale. This opening was filled with a glass tube containing a solution of the red food colour Amaranth (Schultz and Julius 107). This tube also acted as a lens See Fig. VII. Readings were taken by means of flashlight.

## 3. EXPERIMENTAL PROCEDURE

The cell was first filled with chlorine and irradiated for several days. It was then thoroughly evacuated, and after the water had been distilled into the cell in vacuo as previously described, an approximately equimolar mixture of hydrogen and chlorine was let in from the storage flash. (See Fig I) the tap (H,) (Fig VI.) having been previously closed. The storage flash was isolated by two taps (one not shown in Fig. I ). The cell was connected to the glass manometer so that it could be ascertained when the pressure in the cell reached atmospheric. The tap (H,) (Fig. VI.) was then opened, the gas mixture being shut off when the water index reached zero.

The various combinations of filters and diaphragms, described above and given in Tables VII were then introduced in turn. The time in seconds taken for the index to move 1 cm was used as an indication of the velocity of reaction.

Owing to the large volume of the storage flask, a large number of runs could be taken for each volume of mixture stored. The readings were taken as follows: One for each of the four screen filter aperture combinations, the cell was then recharged and a second set taken using a different order of filter aperture combinations. Six such sets of readings were recorded the order of the filter aperture combination being changed each time. Intensity changes were varied in each set, with a fresh charging.

The ratio of the areas of the large and small diaphragms was found to be 200.5:1. The velocity with no screen filter (one hundred percent light intensity) and the small diaphragm was taken as unity. The ratio of any other velocity and the above was called the relative velocity. The results obtained are tabulated in Table VII.

## 4. EXPERIMENTAL RESULTS

The experimental results on the effect of intensity are summarized in Table VII, and calculated as in the following sample calculation.

Sample Calculation. (Table VII, B))

1. The fraction of light transmitted by screen filter as determined by thermopile method IV:7.10.
   $1/1_0$ = 0.01075

2.3. Ratio of areas of apertures $\left(\frac{14.41}{1.015}\right)^2$ = 202.1

4. Resulting intensity. Filter aperture combination
   202.1 X 0.01075 = 2.173

5. Time required for meniscus to travel 10 cm = 29.6 sec.

6. Average Velocity. mm/sec = 3.38

7. Relative Velocity taking A as 1 = 2.11

8. Velocity / Intensity $\frac{2.24}{2.173}$ = 1.03

9. Intensity Range ca = 1;100

# TABLE VII.

## The Effect of Light Intensity

| | A. | B. | C. | D. | E. |
|---|---|---|---|---|---|
| 1 Screen Filter | 100 | 0.01075 | 0.00512 | 0.00216 | 0.001091 |
| 2 Diaphragm (1.015) | 1 | | | | |
| 3.Diaphragm (14.41) | | 202.1 | 202.1 | 202.1 | 202.1 |
| 4 Resulting Intensity | 1 | 2.173 | 1.303 | .4365 | .222 |
| 5 Time in secs (10 cm) | 6.24 | 28.0 | 47.4 | 136 | 332 |
| 6 Average Vel. mm/sec | 1.60 | 3.58 | 2.11 | .735 | .301 |
| 7 Relative Velocity | 1 | 2.24 | 1.32 | .459 | .188 |
| 8 Velocity/ Intensity | 1 | 1.03 | 1.01 | 1.05 | 0.85 |
| 9 Intensity Range ca. | 1:1 | 1:100 | 1:200 | 1:500 | 1:1000 |

## 5. DISCUSSION OF RESULTS

The experimental procedure described above is an improvement over that used by Allmand for several reasons. In the first place the method of preparation and purification of the gases and water, gave purer, more sensitive and more reproducible mixtures.

In the second place the errors of calibration noted by Allmand when using his neutral wedge at points of highest and lowest optical density, were eliminated by the use of screen filters.

In the third place the intensity of the source could be checked simultaneously, with the readings. Finally the smaller cell was more readily thermostated.

Any changes of sensitivity of the mixture in the cell, arising from the liberation of oxygen from the photochemical decomposition of the hypochlorus acid, were ruled out by the method of taking a different order of readings in each separate charging.

The use of the tube of red dye to protect the capillary scale from light was also a considerable improvement in this technique in obtaining the velocity measurements.

## REFERENCES V.

1. Kornfeld and Müller, Z. physik. Chem„ 117, 242 (1925)
2. Chapman, J. Chem. Soc., 125, 1521 (1924)
3. Marshall, J. Phys. Chem,, 29, 1453 (1925)
4. Baly and Barker, J. Chem. Soc., 119, 653 (1921)
5. Wood, Phil Mag., 43, 757 (1922)
6. Allmand and Beesley, J. Chem. Soc., 2693, 1930
7. Jones, J.O.S.A., 16, 259 (1928)

# SECTION VI.

## The Variation of the Quantum Yield With Wave Length

### 1. Introduction.

There had been no direct investigation to obtain the above data, until after the work described herein was under way. Moreover, there exists at present a very marked disagreement with regard to the spectral photosusceptibility (amount of change per unit of incident light) and photosensitivity (amount of change per unit of absorbed light) for the hydrogen-chlorine reaction. The quantum yield and threshold depend of course on the above values.

It was considered that a comparative study of the quantum yield by both the Bunsen-Roscoe and the Bodenstein technique would be of considerable value in view of the divergent views held on this subject.

Besides the improvements in the technique of the Bunsen-Roscoe method mentioned in the preceeding section a number of others were introduced into the experimental procedure described in the following pages.

## 2. Description of Apparatus.

The apparatus used for these experiments was a combination of that employed in Sections IV and V. The complete optical train described in IV was used here, the only difference being that the thermopile was placed between the photographic shutter (F) and the cell (Fig. II). The thermopile was mounted in such a way that it could readily be moved in and out of the light beam. The absorption cell was the same as that described in the previous section and was connected to the capillary indicating tube.

## 3. Experimental Procedure

The light was controlled and measured as in Section IV, and the velocity of reaction measured as in Section V.

### Absolute Measurement of Incident Intensity.

In order to obtain the quantum yield it is necessary to know the number of ergs absorbed per second for a given wave-length. If the incident intensity on the gas is also known, the amount absorbed may be calculated from the extinction coefficient.

The E. M. F. developed by the thermopile used, for a radiation flux of 1 erg/mm$^2$/sec. was known to be 20.05 microvolts. The area of the beam was reduced by the iris diaphragm until it just covered the piles. This area was determined exactly with photographic printing out paper as in V and found to be 28.88 mm$^2$. This area of beam was kept constant throughout.

Instead of varying the diameter of the beam in order to adjust the incident intensity to such a value that the movement of the meniscus would be of a convenient order of magnitude, the screen filters were used. The full energy from the least active wave-length was passed into the system directly and the movement noted. Having measured the rate for the first wave-length, the approximate reduction in intensity to bring the velocity of the meniscus to approximately the above value, was obtained quickly by means of a standard carbon in gelatin wedge. The corresponding set of screens to give this reduction were then placed in screen holders and a comparison of the two rates made as in the previous section. From this procedure the quantities were obtained for evaluating the quantum efficiencies.

## 4. Calculation of Results.

### The Value of 1 Einstein in gram calories.

$$1 \text{ Einstein} = N h v$$

where $n$ = Avogadro's number $6.064 \times 10^{23}$
$h$ = Planck's Constant $6.547 \times 10^{-27}$
$v$ = frequency of the light

Since $\lambda v = c$
Where $\lambda$ is the wave length and
$c$ the velocity of the light .
$2.998 \times 10^{10}$ cm sec$^{-1}$

$$1 \text{ Einstein} = N h \frac{c}{\lambda} \cdot \frac{1}{4.18 \times 10^{7}} \text{ g.cals sec}^{-1}$$

$$= \frac{2.847 \times 10^{7}}{\lambda} \text{ g. cals. sec}^{-1}$$

The values calculated from this relation are given in Table VIII. These values are expressed in g. cals/mole, as it usually means more to the chemist, when considering the relations of chemical reactions and light, to refer to the energy relations in this way.

The values for the quantum yield have been calculated as in the sample calculation and are recorded in table IX.

## TABLE VIII.

### Values of an Einstein for Certain Wave-lengths

| mu | g. cals/sec |
|---|---|
| 365.0 | 78,017 |
| 404.6 | 70,365 |
| 435.8 | 65,328 |
| 465.9 | 61,109 |
| 478.5 | 59,490 |
| 546.1 | 52,136 |
| 549.2 | 51,840 |
| 579.1 | 49,163 |

Sample Calculation for 436 mu.

The following factors when multiplied together give the number of Einsteins absorbed and moles of hydrogen chloride formed.

---

A. Length transversed by meniscus time in seconds. = 5.57

B. Volume of capillary tube unit length $\pi(.90)^2$ = 0.0254

C. Number moles per cc (purified gas) 1/22.400

---

D. Number moles hydrogen chloride formed. = $6.31 \times 10^{-6}$

---

E. Thermopile reading. = 5.05 Microvolts.

F. Incident Radiation on cell $\left(A \times \frac{28.88}{20.05}\right)$ = 7.3 erg/sec.

G. Correction for reflection and absorption of pyrex plate 0.891

H. Number of calories /erg $\frac{1}{4.181 \times 10^7}$

I. Fraction of light absorbed (Calculated from e in table II, d = 20.04 cm)= 0.795

J. Einsteins / g. cal / 65,300

K. Correction for screen filters to reduce $I_0$ = 0.1

L. Time in seconds. = 240

---

M. Nol of Einsteins absorbed = $4.54 \times 10^{-11}$

---

N. Quantum Yield (M) / I 139,000

---

O. Relative Quantum Yield 436 = 1

## TABLE IX.

## Relative and Absolute Quantum Yields.

B - R. Technique

| λ<br>mu | 36.6 | 405 | 436 | 546 | 578 |
|---|---|---|---|---|---|
| A | 1.72 | 1.02 | 5.57 | 2.86 | 0.0 |
| B | 0.0254 | 0.0254 | 0.0254 | 0.0254 | 0.0254 |
| C | $\frac{1}{22414}$ | $\frac{1}{22414}$ | $\frac{1}{22414}$ | $\frac{1}{22414}$ | $\frac{1}{22414}$ |
| D | $1.95X10^{-6}$ | $1.16X10^{-6}$ | $6.31X10^{-6}$ | $3.24X10^{-6}$ | 0.0 |
| E | 10.8 | 7.50 | 5.05 | 4.35 | 12.2 |
| F | 15.5 | 10.8 | 7.30 | 6.31 | 17.6 |
| G | 0.845 | 0.883 | 0.890 | 0.902 | 0.905 |
| H | $\frac{1}{4.18X10^7}$ | $\frac{1}{4.18X10^7}$ | $\frac{1}{4.18X10^7}$ | $\frac{1}{4.18X10^7}$ | $\frac{1}{4.18X10^7}$ |
| I | 1.000 | 0.979 | 0.795 | 0.0018 | 0.000086 |
| J | $\frac{1}{78,000}$ | $\frac{1}{70,400}$ | $\frac{1}{65,300}$ | $\frac{1}{52,100}$ | $\frac{1}{51,800}$ |
| K | 0.01 | 0.01 | 0.1 | 1.00 | 1.00 |
| L | 240 | 240 | 240 | 240 | 24000 |
| M | $9.64X10^{-12}$ | $7.79X10^{-12}$ | $4.54X10^{-11}$ | $1.13X10^{-10}$ | $1.37^{-9}$ |
| N | 202,200 | 148,400 | 139,000 | 28,700 | $<3$ |
| O | 1.45 | 1.07 | 1 | 0.21 | |

## 5. Discussion of Results

The most surprising result of this method was the way in which the experimental results could be repeated, the previous workers using the Bunsen and Roscoe Technique had always complained of marked variations in the photosensitivity of the gases. These abrupt changes were not observed here. The main difference, in the technique of the Bunsen and Roscoe method, between the present investigation and those of the previous workers was in the elimination of oxygen and other impurities, by elimination of the electrolytic preparation of the gases.

It might be anticipated that the very low content of oxygen in the gases in the present work would allow a large yield. However such was not the case, the yield here being lower than in either Allmands[1] and Linds[2] experiments. One would certainly expect that the gases used by them would contain a greater concentration of inhibitors.

To summarize the chief differences between the work herein described and that of Allmand and Lind was a lower quantum yield in the green and a higher one in the near ultraviolet. There does not seem to be any explanation for such differences at the moment. Furthermore, no photosensitivity to the red could be found whatever. A glance at (E) in table IX, however, shows that with such a small extinction coefficient very little action could be expected.

## References VI.

1. Allmand and Beesley, J. Chem Soc, 2693 (1930)
2. Lind and Livingston, J.A.C.S. 52, 593 (1930)

# SECTION VII

## The Variation of Yield with Temperature

(Modified Bodenstein Technique)

### 1. Introduction

The importance of the above question, namely, the variation of the quantum yield with temperature, has been previously fully discussed. Furthermore it was of interest to ascertain what difference, if any, would be found in results obtained by the two methods on similar gas mixtures. The fact that the same degree of thermostating throughout the reaction was not necessary in this Bodenstein Technique, afforded one the opportunity of more readily employing a longer reaction cell. Complicating temperature factors involved in the use of water in the cell, were of course eliminated, Another advantage of this method lies in the fact that by using it, it is possible to handle rates of reaction of considerable difference in magnitude.

The fact that the workers previously employing this technique have confined their attention chiefly to one wave-length (436 m µ) added a further interest. Furthermore up until the early part of the present year, no temperature coefficients had been obtained by this method.

The use of such long reaction cells by us necessitated a considerable modification in the original method. Bodenstein's procedure is to irradicate a mixture for a given length of time, and then to immerse the whole reaction cell in liquid air, freeze out the chlorine and hydrogen chloride, and measure the residual pressure of the hydrogen at liquid, air temperature. A comparison is then made with original pressure, showing the amount of hydrogen used up. The modified Bodenstein technique which was employed here is described in the following pages.

In the same section is also described a simple experiment to re-instigate the finding of Amato[1], namely that there was no reaction at -12 °C.

## 2. Description of Method and Apparatus.

The principle used on this method was to measure the increase in pressure, due to the greater volume of hydrogen chloride formed as compared to the simultaneous loss in chlorine. This principle becomes evident in a consideration of the volume reactions on the following equation:

$$H_2 + Cl_2 = 2\ HCl$$

Thus if a mixture of known chlorine pressure is irradiated, and the chlorine and hydrogen chloride frozen out while the hydrogen is pumped off, the resulting increase in pressure on evaporation of the chlorine and hydrogen chloride is a direct measure of the amount of hydrogen chloride formed. The condensation was carried out by pumping off the hydrogen very slowly through the liquid air trap attached to the cell as shown in Figure VI.. The same result had been effected by condensing out the chlorine and hydrogen chloride in the presence of the hydrogen. However, due to the length of tube, this operation required considerable time (4-6 hours) to make sure all the chlorine had been condensed.

The apparatus was the same as that used in the absorption measurements, the temperature of the cell being maintained by the same heating arrangement. The liquid air trap was sealed on in place of the 0.791 cm cell. The only difference in technique was the method of filling and the use of another reaction cell 20.05cm long (Section V. 2).

For the experiment on the low temperature reaction, a cell, ( Fig. VI. ) replaced one of the above. This was emersed vertically in a freezing mixture, contained in a dewar flask and the light reflected in by means of a mirror, as shown in the diagram. Condensation of water vapour on the surface exposed to radiation was prevented by a small cell sealed on to the first. This was all kept slightly warm by a heating element and was kept evacuated.

### 3. Experimemtal Procedure.

The experiments on the effect of temperature on the quantum efficiency were carried out as follows. The diaphragm monometer and cell were filled with chlorine at atmospheric pressure, and room temperature, the temperature and pressure being noted. The chlorine was then frozen out and hydrogen let in until the pressure reached 380 mm. The cell was then closed off and the chlorine allowed to evaporate. Any error in the hydrogen pressure due to part of the gas being cooled, could be neglected as a considerable difference in pressure range around 380 mm has very little effect on the rate of reaction.

The thermopile was placed in position behind the cell. The reading when the chlorine was frozen out gave the incident intensity on the cell. The method followed was to irradiate the cell according to the same principle described in the last section except that the position of the thermopile was different. The calculations were made in the same manner as before, the values of absorption used being taken from Tables 11-V1. The decrease in concentration of the chlorine could be roughly followed by means of the thermopile behind the cell. The results are summarized in Table X.

The low temperature experiment required a slightly different arrangement namely, the thermopile was employed as in the previous section, a mirror being used to reflect the light down the cell. The only difference in calculations being to take into account another factor, namely the losses at the mirror.

The results for these low temperature calculations are given in Table X..

## 4. Calculation of Results

For the work in this section, the capacity of the glass diaphragm manometer was reduced so that manometer plus cell = 141.3 cc.

The values in table X, have been calculated as given below, the same letters being used.

Sample Calculation $\lambda$ 436, 25°.

A. The volume of HCl formed, calculated from the pressure increase of condensable gases left after the hydrogen had been pumped off through the liquid air trap (6.08 cc).

B. The values under B, were calculated from the data in tables, 11, 111, 1V, V, V1, V11, exactly as in the previous section, and are expressed in tabular form in tables X, X1; and in graphical form in figure 1X.

C. The relative quantum yield.

# Table X.

## The Temperature Coefficient of the Reaction.

| λ | 366 | 405 | 436 | 546 | 578 |
|---|---|---|---|---|---|
| Short tube 20 cm | | | | | |
| 25°A | 1.20 | 0.95 | 6.45 | 2.75 | |
| B | 107.000 | 101.000 | 104.000 | 16.600 | |
| C | 1.03 | 0.97 | 1.00 | 0.16 | |
| 35°A | 1.65 | 1.30 | 9.35 | 8.45 | |
| 50°A | 2.30 | 1.88 | 13.48 | 34.00 | |
| 100°A | 6.63 | 5.71 | 44.60 | 52.40 | |
| Long tube 274.5 cm | | | | | |
| 25°A | | | 10.41 | 7.30[a] | |
| 50°A | | | | 1.15[b] | |
| 100°A | | | | 10.15[c] | 20.5 |
| Short tube 20 cm | | | | | |
| -15°C | | | 1.1 | | |
| 25°C | | | 6.45 | | |

(a) 0.1 Screen filter used

(b) 0.01 " " "

(c) 0.001 " " "

## 5. Discussion of Results.

The advantages of the Bodenstein Technique have been considered in the previous pages. These advantages are well exemplified in the greater ease of obtaining concordant results. An interesting development of this technique would be the use of the absorption method mentioned above to follow the rate of reaction by suitably adjusting these rates by screen filters.

The absolute values of the yield at room temperature, obtained by the Bunsen Roscoe and Bodenstein methods were not in agreement, although the relative values were. However, the value of 104,000 obtained by the second method is in rather good agreement with Bodenstein's value of 110,000. It is difficult to account, at present, for the discrepancies between the results obtained in the two methods. The results with 579 mμ, were not in accord with the recent findings of Dhar, who found the reaction to be photosensitive to infra red.

The observation by Amato that no reaction took place at -12°c was not found here for 436 mμ. On the other hand there was found to be considerable combination at that temperature. The results of the temperature coefficients will be discussed in the general discussion.

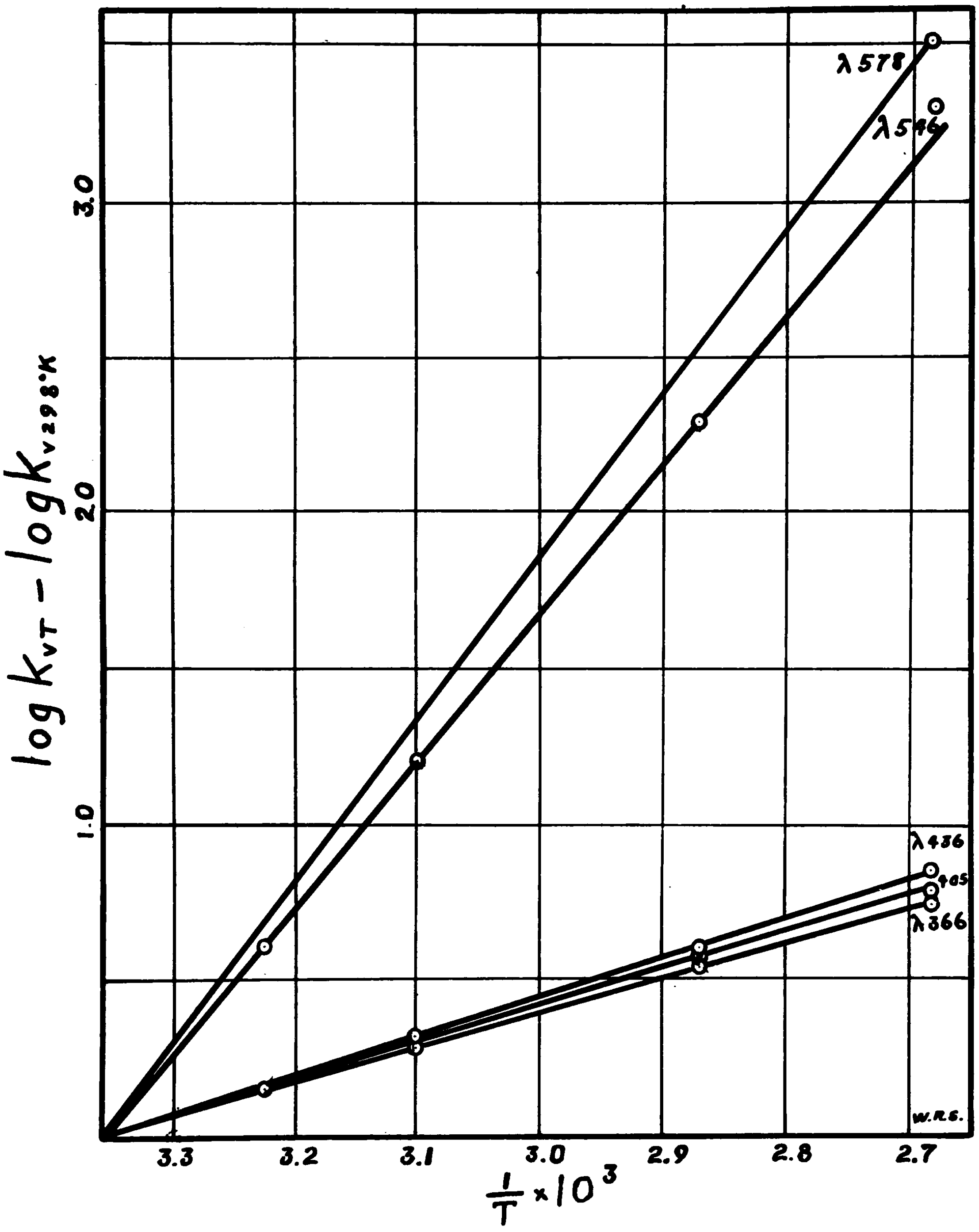
log k_{vT} - log k_{v298°K}
3.0
2.0
1.0
λ578
λ546
λ436
405
λ366
W.R.S.
3.3
3.2
3.1
3.0
2.9
2.8
2.7
1/T × 10^3

Figure IX.

## References Vll.

1. **Amato**, Gazz. chim. ital., 14, 57 (1885)

2. **Bodenstein and Unger**, Z, physik Chem 11, 293, (1931).

3. **Dhar**, The Chemical Action of Light,
Blackie and Son Limited, First edition, 1931.

# SECTION VIII.

## The Effect of the Walls

### 1. Introduction

Practically all theories regarding the mechanism of the hydrogen chlorine reaction bring in a wall effect at some stage. It was thought that further experimental evidence to support such idea would be of use.

The first point to be considered was the effect of a larger area of surface, due to the introduction of powdered pyrex. The second point tested was the effect of covering the wall with sodium chloride. It has been shown by Polanyi and Bogdandy, that in the thermal chain reaction between hydrogen and chlorine, initiated by sodium vapour ($Na + C l_2 = Na Cl + Cl$), the chain length was short when a clean glass surface was present, but increased 30 fold after the glass surface was covered with sodium chloride. It was of interest to see if this effect was also present in the photo-reaction.

## 2. Experimental Procedure and Results.

These experiments were conducted at room temperature as in section Vll, using the 20 cm cell and working at wave length 436 mμ only.

The experiments at atmospheric pressure failed to show any marked difference in the rate, either for the experiment with powdered pyrex or for the one with the walls coated with sodium chloride. However, when the pressure was reduced to 5 mm, the rate was increased six times by the addition of sodium chloride, but only decreased slightly by the action of the pyrex. In the latter case the introduction of nitrogen increased the rate.

These results are summarized in table Xl and are discussed in the section that follows.

## Table Xl.

## The Effect of Walls

$\lambda$ 436, 25°C.

Total pressure 5 mm

| | cc. HCl. |
|---|---|
| No powdered pyrex present | 1.1 |
| Powdered pyrex present | 0.7 |
| Addition of Nitrogen | 1.3 |
| Walls uncovered | 1.1 |
| Walls covered with Na Cl | 6.6 |

# SECTION 1X.

## General Discussion

### 1. Methods

Very little need be said regarding the experimental methods used, as a complete discussion of each was given in the previous pages. However, a brief resume of the main experimental improvements introduced in the present work will be given here.

Improvements in General Photochemical Technique.

(a) The simplified quartz mercury lamp giving great intensities with cooling arrangement was one of the most important factors in the success of the work.

(b) The method using the floating-battery principle for keeping the current on the lamp constant was a very useful improvement in technique.

(c) The method used for measuring the E. M. F's also possessed a great advantage over previously used methods. The results could not have been obtained with nearly the same precision without it.

(d) The use of two monochromators was new in photochemistry, although Jones[1] used it for the photographic plate.

(e) The use of filter screens was not original though it was a comparatively new method. The rocking machine, however, was of original design and the method of blackening the screens a decided improvement.

(f) The use of a silvered lamp with an unsilvered portion for a slit was also an original design.

(g) The simple densitometer was of our own design and had the advantage that it could be readily converted to a microscope again.

(h) Besides the above improvements in apparatus a number of modifications were introduced into the general photochemical technique employed in studying the hydrogen-chlorine reaction, embodied in the use of the combined Bunsen Roscoe and Bodenstein Techniques.

## 2. The Original Work carried out in the present Investigation of the Hydrogen Chloride Reaction.

The following investigations had not been carried out, prior to the present work, on the hydrogen chlorine reaction.

(a) The effect of light intensity over a range greater than 1:440.

(b) The measurement of the temperature coefficient of the extinction coefficient.

(c) The measurement of the temperature coefficient of the quantum efficiency.

(d) A direct demonstration of the effect of yellow light on the reaction, at increased temperature.

(e) The use of the absorption of light by chlorine as a means of following the reaction.

(f) An accurate determination of the photosensitivity at $-15^{\circ}$.

(g) The effect of sodium chloride on the rate of reaction.

## 3. Mechanism of the Reaction.

It is impossible to go into the various theories of the reaction, many of them now of historical interest only, on account of recent work. The procedure followed in this discussion will be to outline what might be termed merely a working hypothesis, in view of the general disagreement prevailing.

A brief outline for reference will be given first. The theories set forth are taken from the work of various experimenters combined with that obtained in the investigation and are merely the author's attempt to summarize briefly the mechanism of the reaction.

As a working hypothesis the following reaction scheme appears to fit most of the facts to date. This reaction is supposed to take place as a chain reaction in a number of stages (which will be referred to as step 1, 2, etc.).

I. $Cl_2 + E = Cl(2\,^{2}P_2) + Cl\ (2\,^{2}P)$,

II. $Cl(\text{or } Cl') + H_2 = HCl + H$,

III. $H + Cl_2 = HCl + Cl$,

IV. $H + O_2 = HO_2$ ........

V. $Cl_2 + O_2 = ClO_2$ .......

VI. $Cl + \text{wall} = 1/2\ Cl_2$,

VII. $Cl + X = Y$ .

Based on the above scheme the latest work of Bodenstein and Unger[2] on the rate of reaction with different concentrations of the gases leads to the following equation , which summarizes best most of the results to date.

$$\frac{d(HCl)}{dt} = \frac{4k_2\ (H_2).(Cl_2).I}{k_6\ \ (Cl_2) + \frac{k_2.k_4}{k_3.k_6}}$$

$$\frac{d(HCl)}{dt} = \frac{4k_2.\ \ \ I.\ (H_2).(Cl_2)}{k_6\ \ (Cl_2) + \frac{k_2.k_4}{k_3.k_6}.(O_2).\ (H_2) + \frac{k_3k_5}{k_2k_4}(Cl_2)}$$

STEP 1. $CI_2 + E = Cl\ (\underset{N}{2^2P_2} - \underset{M}{2^2P_1}).$

Senftleben and Germer[3] demonstrated that when chlorine gas is irradiated by light its thermal conductivity increases. This is taken as evidence for an adiabatic optical dissociation, in contrast to an excited molecule ($Cl_2^1$) type of process. From spectral evidence it appears that chlorine is dissociated into a normal atom (N) and into an excited metastable atom (M).

Chlorine, bromine and iodine vapours show a very complex band structure in the long wave portion of the visible spectrum, the absorption stretching with increasing intensity from the red to the green and thereafter passing over into continuous absorption. The region of continuous absorption is postulated to arise from the absorption of halogen molecules which immediately dissociate, the kinetic energy of the resulting atoms being unquantized. If such is the case we would expect that, in the band spectrum part, the optically excited molecules formed, would revert to the normal form, giving back absorbed energy as a molecular band fluorescence. Such fluorescence should not be observed in the region of the continuum. This was found to be the case of iodine by Dymond[4]. Unfortunately the absorption of chlorine in the band region is very small, and it has not been possible to observe any fluorescence to date.

The existence of a similar dissociation process in hydrogen, is demonstrated by the fall in pressure of hydrogen, on illumination by light of short wave-length, as a result of the absorption of the atoms on the walls of the vessel.

The soundness of the interpretation based on the above spectral evidence originally made by Franck[5], is strengthened, by the close agreement between the heats of dissociation calculated from the above and those determined thermally. The spectroscopic value was obtained from the convergence limit $v_c$ - the term difference, e.g. for chlorine

$$D = hv_c - (2^2P_2 - 2^2P_1) \quad \text{where } \lambda c = 4785^{6,7}$$

$$= 59{,}490 \text{ (Table VIII)} - (2500)$$

$$= 56{,}990 \text{ calories.}$$

The values thus obtained for hydrogen and the halogens is summarized below.

| | SPECTROSCOPIC DATA. | | | HEAT OF DISSOCIATION | |
|---|---|---|---|---|---|
| | | Cal. | $2^2P_2 - 2^2P_1$ | Spectroscopic | Thermal |
| $Cl_2$ | 4785 | 59,490 | 2,500 | 56,990 | 57,000 |
| $Br_2$ | 5107 | 55,800 | 10,500 | 45,300 | 46,200 |
| $I_2$ | 4995 | 57,000 | 21,600 | 35,400 | 35,100 |
| $H_2$ | | | | 100,000 | 105,000 |

At very low pressures the rate of photosynthesis of hydrogen chloride should show a very marked decrease. That is, as the pressure is decreased the number [illegible] returning to the normal state by fluorescence increases, until at such low pressures (1mm) that the time between collisions is long compared to the life period of the excited molecule, fluorescence is practically the only process involved. On the other hand, if the chlorine is dissociated by light the life periods of the atoms are so much longer that such a decrease in rate should not be observed. Rollefson[8] found the velocity constant at these pressures to be independent of the pressure, and decided in favour of the dissociation process.

STEP 11 Cl (or Cl) + $H_2$ = HCl + H

This is the first step in the chain processes postulated. That this reaction has the characteristics of a chain process, is shown by the fact that it possesses all of the seven criteria which are usually assigned to such processes. (Hinshelwood).

For example:

1. In photochemical reaction abnormally large quantum yields are obtained. ( $10^5$ in the above reaction)
2. A retardation of the rate is produced by a change in the dimensions of the vessel, allowing a smaller path for the chains to traverse before reaching the wall. In the ideal case of a chain reaction occurring in a long cylindrical tube, all the chains starting in the gas and being broken at the wall, the rate of reaction should be proportional to the square of the radius of the tube. This was shown to be the case by Trifonov[9] in the above photo-reaction.

3. The acceleration of the reaction, caused in some circumstances by the presence of an inert gas, which keeps the chains off the walls. This phenomenon has been demonstrated in the present work for nitrogen.
4. An abnormal influence of the concentrations of the reacting substances on the rate is observed, due to the fact that the concentrations affect, not only the number of chains starting in unit time, but also the successfulness of their propagation. Recently Trifonov and Rjabinin[10] have reported that the velocity of this photo-reaction at pressure above 0.2 mm, was proportional to the cube of the pressure, in accordance with Semenov's[11] calculations.
5. A rate of reaction is possessed considerably greater than that which might be anticipated from the heat of activation and the collision number.
6. In some cases an abrupt transition takes place, at a certain concentration, from a negligibly slow reaction to an explosion.

Numerous observations dealing with(5 and 6) have been made[12].

Since, as Hinshelwood points out all the above characteristics are not necessarily or even commonly shown by the same reaction, the number found to apply to the hydrogen chlorine reaction is quite remarkable.

The question of whether the normal or the excited atom started the chain in Step II has proved difficult to decide. In recent experiments Rollefson found that iodine chloride is dissociated into normal atoms by the action of light of wave-lengths less than 5774 $A^o$. These will not initiate the chain. He gives this as evidence that chlorine atoms in the excited metastable state $^2P_1$ are necessary for initiation of the chain.

This step is practically thermally neutral. The average value for $\Delta H$ for reaction $2H = H_2$ taken from the work of four [13,14,15,16] independent methods is 103,000 (calculated by the author)

$$\begin{array}{lcll}
2\ H & = & H_2; & \Delta H = -103{,}000\ \text{cals.} \\
2\ Cl & = & Cl_2; & \Delta H = -\ 57{,}000\ \text{"} \\
H_2 + Cl_2 & = & 2HCl; & \Delta H = -\ 44{,}000\ \text{"} \\
\hline
2\ H + 2\ Cl & = & 2\ HCl; & \Delta H = -204{,}000\ \text{"} \\
H + Cl & = & HCl; & \Delta H = -102{,}000\ \text{"} \\
H_2 & = & 2\ H; & \Delta H = 103{,}000\ \text{"} \\
\hline
Cl + H_2 & = & HCl + H; & \Delta H = +1000 \pm 3000\ \text{Cals.}
\end{array}$$

STEP III. $H + Cl_2 = HCl + Cl; \Delta H = -\ 43{,}150.$

Marshall[17] demonstrated the existence of this step by passing atomic hydrogen into $Cl_2$ and measuring the HCl formed. It is considerably endothermic.

STEP IV. $H + O_2 = HO_2$

The existence of such a reaction is demonstrated spectroscopically . The collision of $HO_2$ with H, regenerates the oxygen, thus keeping its concentration constant, as follows

$$H + HO_2 = O_2 + H$$

STEP V. $Cl + O_2 = ClO_2$

Chlorine dioxide has been shown to be an inhibitor[19], in the same sense as $NH_3$. A collision with H or Cl is supposed to regenerate $O_2$ as in step IV.

STEP VI. $Cl + \text{wall} = \frac{1}{2} Cl_2$

Probably more discussion has centred around this step than any other. It also involves the theories of the role of water vapour noted previously.

A number of attempts have been made to measure the life of the chlorine atom by passing a stream of irradiated chlorine under pressure through a capillary at various rates, into hydrogen,[20, 21]. No combination occured. Finally a more direct experiment, employing capillary tubes, was performed by Chapman and Grigg[22], showing that the rate was greatly reduced by the presence of the wall.

The effect of water on the walls on the recombination of atomic hydrogen is known from work with a hydrogen discharge tube[23, 24, 25]. Several experimenters have shown that unless there is a slight amount of water present, rapid recombination takes place. This is believed to occur on the walls.

Polanyi and Bogdandy[26] have demonstrated the effect of sodium chloride on the walls in increasing the yield of HCl in the reaction.

$$Na + Cl_2 = NaCl + Cl$$
$$Cl + H_2 = HCl + H$$
$$H + Cl_2 = HCl + Cl \quad \text{etc.}$$

Furthermore Polanyi and Schay[27] found that in the interaction of sodium vapour and chlorine, the chemiluminescent flame was at first short and of weak intensity, gradually becoming stronger and longer as the surface of the vessel became coated with sodium chloride. As chlorine atoms are common to both the reactions investigated by Polanyi, it appears that it is the recombination of chlorine atoms which is involved at the surface in each case. It has since been demonstrated by Taylor and Lavin[28] that sodium chloride is less efficient than clean glass in promoting the recombination of atomic hydrogen.

In contrast to the last three investigations Pease[29] was able to slow down the rates of the slow reaction between oxygen and hydrogen, and oxygen and hydrocarbons one thousand fold, by covering the glass surface with potassium chloride.

STEP VI[1] $Cl + X = Y$

The fact that the rate of the hydrogen chlorine reaction depends on a power of the intensity of unity and not on the $\sqrt{I}$ as with Bromine atoms[29], is taken to mean that the Cl atoms are removed singly in the gas phase by inhibitors and not by a third body collision (Drierstoss) or on the walls. In the case of bromine atoms in the chain reaction

1. $Br_2 + E = {}_2Br$
2. $Br + H_2 = HBr + H$
3. $H + HBr = H_2 + Br$

and simultaneously

4. $Br + Br = Br_2$

2 in the above is endothermic (heat of activation 17,000cals) and the bromine atoms are not used up as efficiently as in

the case of the hydrogen chlorine reaction. Hence much recombination occurs. The rate of reaction (2) with hydrogen is proportional to the concentration of bromine atoms at any instant. Since the rate of dissociation is proportional to $(Br_2)$ x Intensity and the rate of recombination to $(Br)^2$ it follows that the concentration of (Br) and hence the rate (2) is proportional to $\sqrt{(Br_2) \times \text{Intensity}}$. In contrast to this, the chlorine atoms are used much more efficiently by Step II, resulting in little recombination, and hence the direct proportionality with light intensity.

The observation that the Töpler Striae occurring in the experiments of Weigert and Kellerman[30], are only seen on the exact coincidence of the beam, has been interpreted to mean that all the reaction takes place in the beam. However it is possible that what they get with such striae is the Budde Effect.

Using oxygen free gases, Bodenstein and Unger came to the conclusion, that there was a volatile compound diffusing from the walls. They believe this to be a silicon chloride or oxychloride formed by the reaction of chlorine atoms on the walls.

## The Order of the Reaction.

The classification of this reaction into a definite order is not of much significance because in the first place it is a chain reaction and in the second it is a photo-reaction, the order of which is a function of the light absorption.

If we consider the single step I the photo-decomposition of chlorine, and assume that the reaction is irreversible and the rate proportional to the light intensity, the following expression has been derived by Wegschieder[31] for such a case.

$$\frac{k.\alpha.\ I_0.\ q.\ S.\ t}{V} = \alpha S x + \log_e .\ \frac{1 - e^{-a\ S\ a}}{1 - e^{-a\ S\ (a-x)}}$$

where $k$ = quantum yield (2 above)

$\alpha$ = molecular absorption coefficient,

$I_0$ = incident light intensity,

$q$ = cross sectional area of the beam,

$S$ = length of the beam,

$t$ = the term,

$V$ = volume of the reaction mixture,

$a$ = initial concentration of chlorine,

and $a-x$ = concentration at time t.

For the limiting case of strong light absorption ($\alpha S x$ large) second term on the right hand side of the equation approaches log 1 and may be neglected, and

$$x = \frac{k.\ I_0.\ q.\ t}{V}$$

or the amount of change is proportional to the time (zero order reaction).

On the other hand for the case of weak absorption, $\alpha S x$ becomes very small and may be neglected.

Hence $$\frac{k.\ \alpha.\ I_0\ \ q.\ S.\ t}{V} = \log_e \frac{1 - e^{-aSa}}{1 - e^{-aS\ (a - x)}}$$

taking only the first two terms in the series:

$$(e^{-x} = 1 - x + \frac{x^2}{2})$$

$$= \log_e \frac{1 - 1 + a.\ S.\ a.}{1 - 1 + a.\ S.\ (a - x)}$$

we have

$$\frac{k.\alpha I_0.q.S}{V} = \frac{1}{t} \log_e \frac{a}{a - x}\ .$$

the equation for a unimolecular reaction . Hence, for chlorine we have both the limiting cases ( λ 366 and 578 mμ) and a number of intermediate cases.

When it is remembered that one or both of the atoms in the above decomposition can initiate a chain, the term order of the reaction soon loses its significance.

## Temperature Coefficient of Light Absorption.

The temperature coefficient of light absorption appeared in this work to follow an Arrhenius equation exactly for wave-lengths 366, 405 and 436 mμ, falling off slightly at the higher wave-lengths, 546, 578.

## The Quantum Yield for Different Wave-Lengths.

It is believed that these experiments gave quite an exact measurement of the quantum yield. There seems to be no reason, a priori, why the yield in the presence of a layer of water should be greater, than with the tube just wetted as in the Bodenstein experiment. Of course there is a possibility that the water may lower the concentration of X ($VI^1$); or that sufficient water vapour was not present to cover the walls, although as stated earlier, precautions were taken to have sufficient water vapour present. It would appear to the author that, if anything, the yield with water present should be smaller, due to the liberation of oxygen from the photo-decomposition of HClO. However there appear to be some grounds for believing that the water is advantageous, because Allmand[32] reports a maximum yield of 500,000 and Lind[33] a maximum of 170,000 using the B-R. Technique. While Bodenstein obtained a yield of 110,000 with pure hydrogen and chlorine. Of course there may be an effect due to the water surface similar to the catalytic effects found by Maass and Sutherland[34] for liquid surfaces, or the reduction of the area of glass exposed by the addition of the water, may have been a contributing factor.

Allmand obtained his maximum relative yield at 405 mμ, against our maximum at 366 mμ. It is significant to note that two of the most direct experiments planned to study the effect of 546 mμ both gave positive results (Allmand and Sawyer). At room temperature no reaction to the red or infra-red could be obtained. This result is in contrast to the findings of Dhar[35].

The values of the yield together with the temperature coefficients of the light absorption and reaction are given in table XII.

## TABLE XII.

The temperature coefficients of the reaction (25-35°); the temperature coefficients of the light absorption (25-35°); the absolute and relative quantum yields.

| $\lambda$ | 366 | 405 | 436 | 546 | 578 |
|---|---|---|---|---|---|
| $\frac{d\ ABS}{d\ T} =$ | 1.01 | 1.04 | 1.08 | 1.58 | 1.8 |
| $\frac{d\ \log kv}{dT} =$ | 1.37 | 1.40 | 1.48 | 4.10 | |
| B-R-T | | | 139,000 | | |
| Rel. $\gamma$ | 1.45 | 1.07 | 1.00 | 0.21 | |
| Bod T. | | | 104,000 | | |
| | 1.03 | 0.97 | 1.00 | 0.16 | |

## Temperature Coefficients of the Quantum Yield.

The temperature coefficients (total) appeared to follow an Arrhenius curve for the lower wave-lengths, as did the absorption (fig IX). It is thus believed that at wave-lengths 365, 405, and 436 mµ, there are two factors, following this curve, namely, the absorption, and a temperature coefficient of some step in the thermal chain. At λ 546 mµ the total temperature coefficient increased relatively more rapidly than the corresponding coefficient of the absorption. A possible explanation may arise from the fact that the fraction of the light absorbed in the continuum may increase with rise of temperature.

$$\frac{\text{Abs. Cont.}}{\text{Abs. Cont.} + \text{Abs. band}}$$

The absorption spectrum of chlorine in the visible is divided into four parts. The first showing a band spectra with maximum at about 643, then a region of very little absorption, followed by another band spectrum, developing into a continuum at 478.5 m µ.

Figure X, shows the absorption near λ 500 mµ. At the bottom of the figure are shown, separated out the

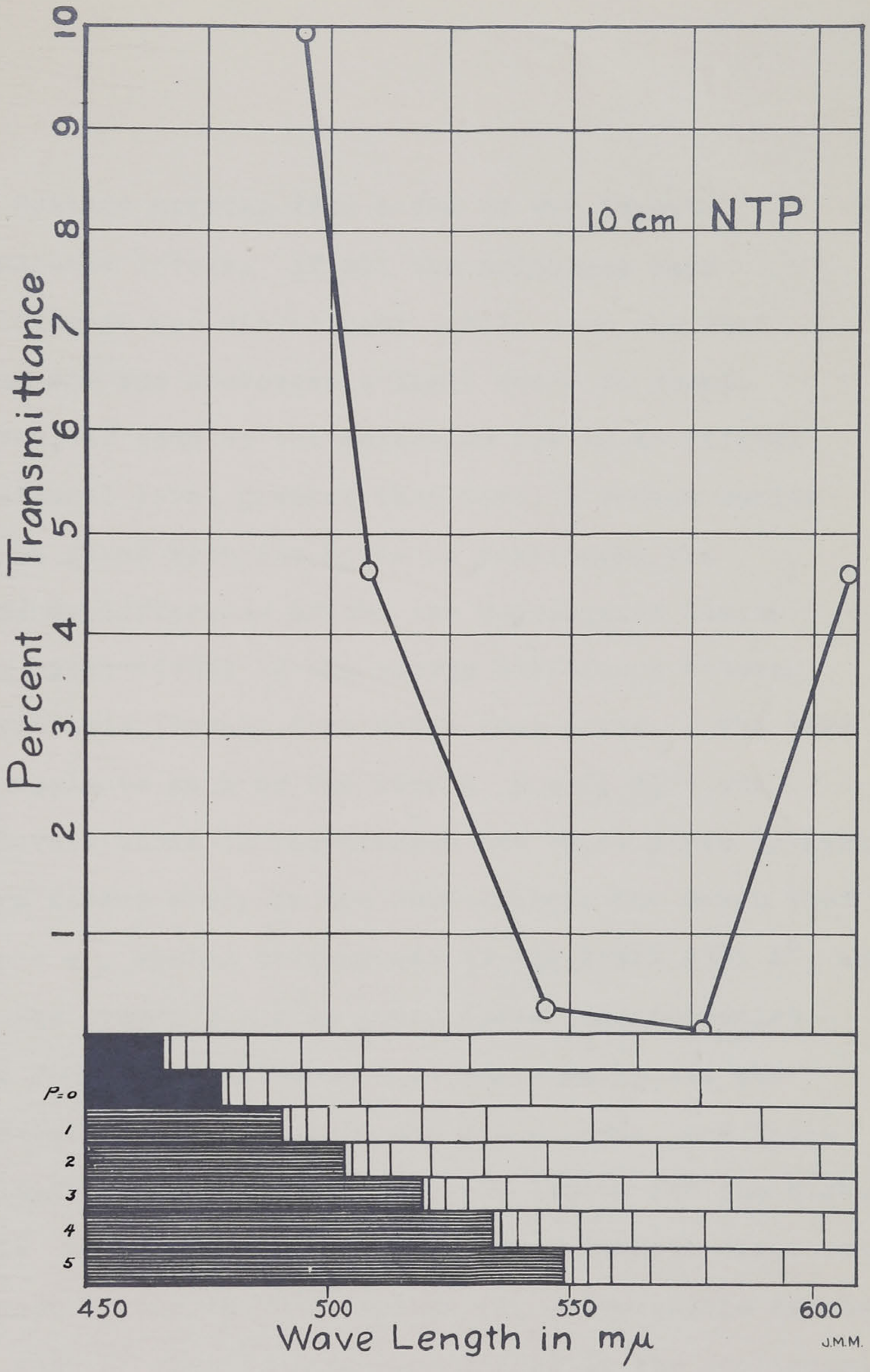
10 cm NTP
Percent Transmittance
10
9
8
7
6
5
4
3
2
1
P=0
1
2
3
4
5
450
500
550
600
Wave Length in mμ
J.M.M.

Figure X.

band systems arising from a few of the lowest vibrational levels. If all the molecules were initially in one vibrational level, just one band system and one convergence limit would be found. However, if some of the molecules are in an initial vibrational level greater than zero, a second series will be found with its appended continuum, the frequency difference of the two convergence limits being proportional to the energy difference between the vibration levels from which they arise. The same will apply to each of the levels $p = 2, 3, 4$ etc. The levels shown in the diagram are those given by Kuhn. A more recent study by the same author, has shown that the $p = o$ , system corresponds to the limit 4785 A°, and that the system $p = o'$ as given above does not exist. It is found with chlorine that practically all the molecules are initially in the $p = o$ level, and hence the limit observed is at 4785, the limits for the higher levels being too faint. Thus for adiabatic dissociation for most of the chlorine molecules, wave-lengths shorter than 4785 A° should be necessary (inside the continuum). However there will be a number initially in the higher levels and these will then require a smaller amount of energy for dissociation. The fraction in each level is given approximately by the Boltzman quota, $e^{-\frac{nE}{RT}}$, E being the energy associated with the nth level.

Although the fraction in the upper levels is small at room temperature it increases very rapidly with the temperature, and hence the bands p = 1, 2, 3 etc increase in intensity. This accounts for the increase in absorption with the temperature.

The fact that the quantum yield increases with temperature relatively faster than the light absorption, is probably due to only part of the energy, which was measured by the thermopile method, being in the continuum. $\left( \frac{\text{Abs.cont.}}{\text{Abs. cont.} + \text{Abs. band}} \right.$

As the temperature increased this fraction became larger and hence the quantum yield increased.

In figure IX it is shown that the temperature coefficient increased with wave-length in qualitative agreement with Tolman's Equation. By a statistical mechanical treatment Tolman[38, 39] arrived at the following expression, for a bimolecular photochemical reaction,

$$\frac{d \ln k_\nu}{d T} = \frac{1}{2T} + \frac{e''_A - e'_A + e''_B - e'_B}{R T^2} .$$

in which the temperature coefficient for a given frequency is equated to the energies of the molecules concerned as follows: $e''_A$ is the average energy of those molecules of kind (A) which absorb the light and react; $e'_A$ is the average energy of all the molecules of kind (A); $e''_B$ is the average energy of the molecules of kind (B) which react with the activated molecules (A); $e'_B$ is the average energy of all the molecules of kind B. The term $e''_B - e'_B$ is the temperature coefficient of the thermal reaction. In the case of the hydrogen-chlorine reaction it may be the temperature coefficient of one of the steps in the chain. The value 1.36 (25-35°) for the chain corresponds to a heat of activation of 5600 cals. It might therefore be due to the reaction which destroys the inhibitor

When the above expression is differientiated with respective to frequency, we get

$$\frac{d.}{d\nu} \left( \frac{d \ln k_\nu}{d T} \right) = \frac{1}{RT^2} \cdot \frac{d e''}{d\nu}$$

Thus, according to the equation the temperature coefficient should increase with the wave-length, if the average energy of the molecules which absorb the light and react decreases with temperature.

We found this to be the case, the temperature coefficients for $\lambda$436 and 546, being 1.48 and 4.10 respectively.

It is difficult to compare data on the temperature coefficient because it varies with the sensitiveness of the mixture, as well as with the value of the extinction.

Lind and Livingston found that the temperature coefficient of reaction initiated by white light and by $\alpha$ particles was the same namely 1.20; that it increased with the chain length equally for both; and that for green light it increased to 1.29. They postulated that the whole of the temperature coefficient arose from the thermal reaction, neglecting any increase due to increased absorption. Allmand in calculating the temperature coefficients of his quantum yield also assumed the coefficient of absorption to be unity.

In conclusion it may be said that what is needed most at the present time for the elucidation of the mechanism of the photosynthesis of hydrogen chloride is much more experimental evidence.

## References IX.

1. Jones and Sandvik, 12, 401 (1926)
2. Bodenstein and Unger, Z. physik. Chem, B, 11, 253 (1931)
3. Senftleben and Germer, Ann. Physik. 2, 847 (1929)
4. Dymond, Z. physik., 34, 553 (1925)
5. Franck, Trans. Faraday Soc., 21, 536 (1925)
6. Kuhn, Z. Physik, 39, 77 (1926)
7. Turner, Physics Rev., 27, 397 (1926)
8. Rollefson and Lindquist, J.A.C.S. 52, 2793 (1930)
9. Trifonov, Z. physik. Chem., 313, 195 (1929)
10. Trifonov and Rjabinin, ibid., 6, 118 (1929)
11. Semenov, Z. physik., 48, 571 (1928)
12. Mellor, Comp. Treatise Inorganic and Theoretical Chemistry, Longmans Green and Company, Vol.11(1922)
13. Condon, Proc. Nat. Acad. Sci., 13, 466 (1927)
14. Bodenstein and Jung, Z. physik. Chem.,121, 127 (1926)
15. Bichowsky and Copeland, J.A.C.S., 50, 1315 (1928)
16. Whitmer, Proc. Nat. Acad. Sci, 12, 238 (1926)
17. Marshall, J. Phys. Chem., 29, 842 (1925)
18. Urey, Dawsey and Rice, J.A.C.S., 51, 1371 (1929)
19. Chapman and McMahon, J. Chem. Soc., 97, 845 (1909)
20. Bodenstein and Taylor, Z. Electro. Chem., 22, 202 (1916)

21. Marshall, J. Phys. Chem., 30, 757 (1926)

22. Chapman and Grigg, J. Chem. Soc., 2426 (1929)

23. Wood, Proc. Roy. Soc., 102A, 1 (1923)

24. Marshall, J. Phys. Chem., 29, 1453 (1925)

25. Bonhoeffer, Z. Physik. Chem., 29, 1453 (1925)

26. Polanyi and Bogdandy, Z. Electro. Chem., 22, 202 (1916)

27. Polanyi and Schay, Z. physik. Chem., B,L, 30 (1928)

28. Taylor and Lavin, J.A.C.S., 52, 1910 (1930)

29. Pease, J.A.C.S., 51, 1839 (1929)

30. Weigert and Kellerman, Z. physik. Chem, 107, 1 (1924)

31. Wegschieder, Z. physik. Chem., 103, 273 (1923)

32. Allmand and Beesely, J. Chem. Soc., 2693 (1930)

33. Lind and Livingston, J.A.C.S., 52, 593 (1930)

34. Sutherland, Diss., McGill, 1931.

35. Dhar and Bhagwatt, Z. f. Anorg. Chem. ,190, 415 (1930)

36. Kuhn, Z. physik., 39, 77 (1926)

37. Eliot, Proc. Roy. Soc., A127, 638 (1930)

38. Tolman, J.A.C.S., 42, 2506 (1930)

39. Tolman, ibid, 45, 2285 (1923)

# SECTION X.

## SUMMARY

1. The importance of photochemistry and its relation to the study of chemical kinetics has been discussed.
2. A brief historical review has been given for the photosynthesis of hydrogen chloride in particular.
3. An experimental study of the photosynthesis of hydrogen chloride has been made using both a modified Bunsen-Roscoe and a modified Bodenstein Technique with certain improvements.
4. A number of improvements in the general technique of photochemistry have also been introduced.
5. The effect of temperature on the extinction coefficients of chlorine has been obtained for wave lengths 365, 405, 436, 546 and 578 m μ.
6. Data have been obtained on the effect of following factors, light intensity, wave-lengths, temperature, and walls, on the quantum yield.
7. A working hypothesis of the mechanism of the reaction has been discussed.

8. It has been concluded that quanta too small ($\lambda$ 578) to activate chlorine at room temperature, become effective in activating molecules already partially activated by an increase in temperature ( 25 - 100°C.)

9. A complete summary of 4, 5, 6 and 7 has been given at the beginning of the general discussion.

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