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PHOTOCHEMICAL PROCESSES

BY

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American Chemical Society
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GENERAL INTRODUCTION

American Chemical Society Series of Scientific and Technologic Monographs

By arrangement with the Interallied Conference of Pure and Applied Chemistry, which met in London and Brussels in July, 1919, the American Chemical Society was to undertake the production and publication of Scientific and Technologic Monographs on chemical subjects. At the same time it was agreed that the National Research Council, in coöperation with the American Chemical Society and the American Physical Society, should undertake the production and publication of Critical Tables of Chemical and Physical Constants. The American Chemical Society and the National Research Council mutually agreed to care for these two fields of chemical development. The American Chemical Society named as Trustees, to make the necessary arrangements for the publication of the monographs, Charles L. Parsons, Secretary of the American Chemical Society, Washington, D. C.; John E. Teeple, Treasurer of the American Chemical Society, New York City; and Professor Gellert Alleman of Swarthmore College. The Trustees have arranged for the publication of the American Chemical Society series of (a) Scientific and (b) Technologic Monographs by the Chemical Catalog Company of New York City.

The Council, acting through the Committee on National Policy of the American Chemical Society, appointed the editors, named at the close of this introduction, to have charge of securing authors, and of considering critically the manuscripts prepared. The editors of each series will endeavor to select topics which are of current interest and authors who are recognized as authorities in their respective fields. The list of monographs thus far secured appears in the publisher's own announcement elsewhere in this volume.

The development of knowledge in all branches of science, and especially in chemistry, has been so rapid during the last fifty years and the fields covered by this development have been so varied that it is difficult for any individual to keep in touch with the progress in branches of science outside his own specialty. In spite of the facilities for the examination of the literature given by Chemical Abstracts and such compendia as Beilstein's Handbuch der Organischen Chemie, Richter's Lexikon, Ostwald's Lehrbuch der Allgemeinen Chemie, Abegg's and Gmelin-Kraut's Handbuch der Anorganischen Chemie and the English and French Dictionaries of Chemistry, it often takes a great deal of time to coördinate the knowledge available upon a single topic. Consequently when men who have spent years in the study of important subjects are willing to coördinate their knowledge and present it in concise, readable form, they perform a service of the highest value to their fellow chemists.

It was with a clear recognition of the usefulness of reviews of this character that a Committee of the American Chemical Society recommended the publication of the two series of monographs under the auspices of the Society.

Two rather distinct purposes are to be served by these monographs. The first purpose, whose fulfilment will probably render to chemists in general the most important service, is to present the knowledge available upon the chosen topic in a readable form, intelligible to those whose activities may be along a wholly different line. Many chemists fail to realize how closely their investigations may be connected with other work which on the surface appears far afield from their own. These monographs will enable such men to form closer contact with the work of chemists in other lines of research. The second purpose is to promote research in the branch of science covered by the monograph, by furnishing a well digested survey of the progress already made in that field and by pointing out directions in which investigation needs to be extended. To facilitate the attainment of this purpose, it is intended to include extended references to the literature, which will enable anyone interested to follow up the subject in more detail. If the literature is so voluminous that a complete bibliography is impracticable, a critical selection will be made of those papers which are most important.

The publication of these books marks a distinct departure in the policy of the American Chemical Society inasmuch as it is a serious attempt to found an American chemical literature without primary regard to commercial considerations. The success of the venture will depend in large part upon the measure of coöperation which can be secured in the preparation of books dealing adequately with topics of general interest; it is earnestly hoped, therefore, that every member of the various organizations in the chemical and allied industries will recognize the importance of the enterprise and take sufficient interest to justify it.

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PHOTOCHEMICAL PROCESSES

CHAPTER I

THE CONCEPT OF LIGHT QUANTA AND PHOTOCHEMICAL KINETICS

Photochemistry is relatively a very young science. Thus, although occasional observations of the chemical effects of light can be found mentioned already in manuscripts dating from the classical era of human history and although, in subsequent periods, such observations were considerably multiplied, only in the nineteenth century was the first and fundamental law of photochemistry deduced.

Grotthuss published in 1817 a paper which contained a clear outline of this law. As formulated by him, the law states that only light which is absorbed can produce chemical change. Grotthuss' paper attracted little attention on the part of his contemporaries, and in 1839 Draper derived independently the same law and supported it by experiments on the hydrogen chlorine reaction.

Bunsen and Roscoe found by investigating the same reaction that, when the product of light intensity and time was kept constant,

$$I \times t = \text{const},$$

the amount of hydrogen chloride formed also remained unchanged. They generalised this observation in a law, assumed to hold for all photochemical processes. Bunsen and Roscoe also demonstrated the validity of Lambert's and of Beer's laws of light absorption for light sensitive mixtures. They, however, still believed that a photochemically reacting mixture might show a different light absorption from that of its pure components. This difference was assumed to be due to the reaction and was called "the photochemical extinction of light."

It is convenient to recapitulate briefly here some of the laws of optics which have an immediate bearing on photochemistry from the point of view of the Grotthuss-Draper law. If radiant energy enters a material medium, a certain fraction of it is reflected by the surface r, another fraction is in general absorbed by the medium a. These

fractions of the incident energy are related to that fraction which passes through the medium t by the equation:

$$r + a + t = 1.$$

Fresnel's Law. The amount of light energy reflected at the boundary of two optical media will be in general dependent on the angle of incidence of the light. For the case of an ideal plane surface and perpendicular incidence, the law of Fresnel states that the fraction reflected is given by the equation

$$I_r = \left(\frac{n-1}{n+1}\right)^2 I_{inc},$$

where n is the ratio of the refractive indices of the two media.

The real surfaces, not being perfectly plane, show, besides the regular reflection given by the formula, also the effect of light scattering. The total amount reflected is therefore generally larger than that given by Fresnel's equation.

Lambert's Law. The amount of radiant energy absorbed in a *homogeneous* medium follows from Lambert's law:

$$I_x = I_o \; e^{-\beta x}$$

where I_o and I_x denote the initial and final light intensities, x is the thickness of the layer and β is the specific light absorption coefficient. The fraction of light energy absorbed by a medium of a layer thickness x is therefore:

$$(1 - e^{-\beta x}).$$

Beer's Law. As a special case of Lambert's equation may be considered the law of Beer, which states that the absorption coefficient β is proportional to the concentration, c, of a light-absorbing substance, $\beta = ac$. The expression for the light absorption becomes therefore

$$I_{abs.} = I_{entering} \; (1 - e^{-acx})$$

The laws of Lambert and Beer are valid only for monochromatic light, since, in general, the absorption coefficients β and a vary with the wave length of incident light. Besides the monochromatic nature of the light, the law of Lambert presupposes only the homogeneity of the medium, whereas, in the law of Beer, certain assumptions as to the independence of the optical properties of substances as regards their concentration are included. Accordingly, we find that several deviations from this last law have been recorded in the literature.

Light Scattering. The substances used for photochemical experiments are very seldom "optically clear" and the suspended small par-

ticles show the effect of light scattering. With some colloidal solutions the intensity of light scattering may increase to such dimensions that, although no light is transmitted, only a small fraction of it is actually absorbed, the rest being scattered. The studies of Lord Rayleigh demonstrated that the scattering power is very often inversely proportional to the fourth power of the wave length of the incident light.

Photo-Kinetics. For more than half a century following the fundamental studies of Draper, and Bunsen and Roscoe very little advance in the theoretical treatment of photochemistry was registered. The amount of experimental material increased, however, enormously and more quantitative methods dealing with photochemical reactions were developed. The rapid development of chemical kinetics and statics, due to the mass action law and the application of thermodynamics, resulted in experiments designed to apply the same principles to theoretical photochemistry. We find in older editions of Nernst's "Theoretical Chemistry" an equation for the rate of photochemical reactions

$$\frac{dc_1}{dt} = k\ c_1^{n_1}\ c_2^{n_2}\ c_3^{n_3} \ldots\ldots$$

in which the coefficient k was supposed to be a function of the light intensity, the equation being otherwise an expression of the mass action law.

This equation, being in apparent disagreement with the Grotthuss-Draper law, yields, however, results which are, at least formally, consistent with it, since the coefficient k was supposed to be a local function in those photochemical systems, where the light intensity, due to absorption, decreased from layer to layer. Wilderman, Byk, Weigert, tried to treat photochemical reactions on the basis of classical thermodynamics. These attempts can hardly be considered as successful and they have now only historical interest. Several theories of photochemical reactions have been developed by Luther, by Lasareff, by Plotnikoff and by others which are all based on a quantitative formulation of the Grotthuss-Draper law as suggested originally by van't Hoff. Van't Hoff assumed that the rate of photochemical reactions is determined by the amount of absorbed light energy and is proportional to it, thus to the quantity:

$$I_{abs} = I_0\ (1 - e^{-acx})$$

if the radiation is monochromatic. If a, c and x of this expression are large, then practically complete light absorption takes place; I_{abs}

is thus constant and the reaction rate must be independent of the concentration of the light absorbing component. If, on the other hand, the reaction is studied in an infinitely thin layer or a and c (the concentration) are small, then the above expression is reduced to

$$I_{abs} = I_0 \alpha c x$$

and, accordingly, the reaction must be unimolecular with respect to the light absorbing component. These two extreme cases were found to be in good agreement with experimental results available at that time, but the known dependence of several reactions on the concentration of the non-absorbing components required additional assumptions. The whole treatment was therefore somewhat formal, since the main kinetic question: why on illumination only certain molecules of the light absorbing component reacted and not its whole mass at once, could not be answered satisfactorily.

Light Quanta. A starting point for the rapid development of photochemistry along new lines was undoubtedly the introduction of quantum theory. General attention turned from rather unsuccessful thermodynamic speculations to a quantitative study of photochemical kinetics, resulting in a deeper understanding of the rôle of radiant energy in producing chemical changes and in many valuable contributions to the general theory of chemical kinetics.

An analysis of the modern literature on the subject shows that by far the larger proportion of all the theoretical and experimental photochemical studies in the course of the last fifteen years have been connected to some extent with Einstein's equivalence law, and, though it soon became apparent that this is by no means an exact law governing all photochemical reactions, nevertheless, the idea of light absorption according to quantum laws, applied to photochemistry, proved to be at least a most useful working hypothesis.

Moreover, the study of photochemical reactions gained, by application of the equivalence law, subsequently discussed in detail, an important advantage over that of thermal reactions. Whereas these latter meet difficulties in solving two main kinetic problems: how many and from what sources of energy activated molecules are formed in the course of a reaction and how do they react, photochemistry has a ready answer to the first of these questions, in so far as the assumptions of the equivalence law be accepted.

Accordingly, an answer to the second question can be sought and found in a more satisfying manner and, actually, up to the present

time, the kinetics of several photochemical reactions have obtained in this way a more or less definitive explanation.

However, only little has yet been done in this direction, and photochemical kinetics is still an open field of study, which, in the coming years, should yield many contributions to the general problem of the properties of matter.

Stark's Formulation of Quantum Processes. The first idea of the application of the quantum theory to photochemical reactions belongs to Stark [1] who, from considerations on atomic and molecular structure, was led to the assumption that, in certain cases, the rate of photochemical change is determined by the number of absorbed light quanta. His whole theory, being expressed in a somewhat general form, did not obtain much consideration from photochemists. In addition to this somewhat indefinite formulation of the equivalence law, Stark drew a clear distinction between the primary and secondary stages of a direct photochemical change and an equally clear distinction between the mechanism of direct and indirect (including sensitised) reactions.[2]

Einstein's Equivalence Law. An exact formulation of the conditions necessary for the application of the quantum theory to chemical reactions is due to Einstein [3] whose first derivation of the so-called equivalence law is based solely on classical thermodynamics and Planck's radiation law. This derivation was given and is strictly valid only for a very special type of an ideal photochemical reaction: a completely reversible thermodynamic equilibrium between the black body radiation and a chemical system $AB \rightleftarrows A + B$; AB being decomposed on absorption of radiation of a characteristic frequency ν and this frequency being emitted in the reverse reaction $A + B \longrightarrow AB$, which is assumed to be uninfluenced by radiation. Einstein showed that the introduction of radiation of the frequency ν, of a higher density (temperature) than that of the "dark" equilibrium, into this system, must result in a shift of equilibrium to the side of decomposition and that the decomposition of N molecules of AB requires the absorption of light energy in amount equal to $Nh\nu$, where h is Planck's constant.

In the next paper, Einstein [4] extended the derivation of the equivalence law to the case that a finite frequency interval $d\nu$ is effective, other assumptions being unchanged. Later, Einstein [5] took up the

[1] *Physik. Z.*, 9, 898 (1909).
[2] Allmand, *Trans. Farad. Soc.*, 21, 438 (1926).
[3] *Ann. Physik*, 37, 832 (1912).
[4] *Ibid.*, 38, 881 (1913).
[5] *Ber. deutsch. physik. Ges.*, 18, 315 (1916).

problem again treating it from a different angle. In this the Bohr atom and light absorption in discontinuous energy quanta were assumed as the basis of the whole calculation. The assumption was further made, that, at a sufficiently low temperature, practically all the light absorbing molecules of a photochemical system are in the lowest quantum state. From these assumptions Einstein deduced that absorbed light energy in amount equal to $Nh\nu$ should bring to reaction N molecules, provided the time interval between the absorption of an energy quantum by a molecule and its subsequent reaction was small in comparison with the mean life of activated molecules, i.e., with the time interval between absorption and re-emission of light energy by a molecule.

Bodenstein's Calculations. Bodenstein,[6] stimulated by the theoretical considerations of Stark, calculated the quantum yield, or the number of reacting molecules per absorbed light quantum, of several reactions which had been studied quantitatively. These calculations were only of an approximate character, since no direct measurements of the light energy absorbed in different photochemical reactions were available at that time. He deduced the different values by comparison of the geometrical arrangement in varied experiments with the partially known absorption spectra of the reacting substances and with the known energy distribution in the emission spectra of the light sources used.

Bodenstein came to the conclusion that, whereas a part of the photochemical reactions proceeded at a rate which was very close to that calculated from the equivalence law, some of them decidedly contradicted it (see Table 1).

Discussing the possible causes of these deviations, he concluded that what is observable as the rate of a photochemical reaction is, in reality, the combined effect of a whole sequence of reactions of which only the first one—the primary photochemical process—is directly released by absorption of light energy.

According to Bodenstein, the equivalence law strictly determines the rate of all primary photochemical processes. The secondary reactions depend, of course, on the chemical constitution of a photochemical system. Bodenstein assumed further that their partial rates are determined by the mass action law.

Applying these principles to the calculation of the total rates of photochemical reactions, Bodenstein demonstrated that expressions could be derived which were in good agreement with the experimental

[6] *Z. physik. Chem.*, 85, 329 (1913). Comp. also Winther, *Z. wiss. Phot.*, 11, 92 (1913).

TABLE 1.

Reaction	Molecules reacting / Quanta absorbed
Polymerisation of anthracene	0.3 – 1.4
Decomposition of laevulose	0.7
$C_6H_4NO_2CHO \rightarrow C_6H_4NOCOOH$	0.1
Polymerisation of sulfur ($S\lambda \rightarrow S\mu$)	0.2
Oxidation of quinine by chromic acid	0.7
$2O_3 \rightarrow 3O_2$ (in presence of chlorine)	0.6 – 1.3
$3O_2 \rightarrow 2O_3$	1.
$2NH_3 \rightarrow N_2 + 3H_2$	0.25
$H_2 + Cl_2 \rightarrow 2HCl$	10^6
$2O_3 \rightarrow 3O_2$	10^3
Hydrolysis of acetone	2×10^3
$C_2O_4H_2 \rightarrow CO_2 + CO + H_2O$ (in presence of uranyl nitrate)	5×10^4
Hydrolysis of chloroplatinic acids	1.
$2H_2O_2 \rightarrow 2H_2O + O_2$	10^2
Oxidation of quinine by oxygen	5×10^{-1}
Bleaching of dyes	2 to 5×10^{-3}
$4HI + O_2 = 2H_2O + 2I_2$	10^6
Oxidation of iodoform by oxygen	1 – 15
$CO + Cl_2 \rightarrow COCl_2$	10^3
$Br_2 + C_6H_5CH_3 \rightarrow C_6H_5CH_2Br + HBr$	10^6

results. The kinetic theory assumed by Bodenstein, which involved a primary ionisation of molecules on light absorption and subsequent reactions induced by free electrons, proved to be invalid, since no ionisation on illumination could be in general observed (excepting a few special cases in short ultraviolet light); but the importance of Bodenstein's work lies in the definite acceptance of the equivalence law and in the explanation, on the basis of kinetic calculations, of the causes of deviations from this law.

In the years following Bodenstein's publication different kinetic theories of photochemical reactions were occasionally advanced. We shall note that several of these theories are developed along similar lines to that of Bodenstein, and the equivalence law is considered as strictly valid for the primary process. In other theories no clear distinction is drawn between the primary and secondary processes, and known deviations from the equivalence law are explained by assuming the usual quantum laws of light absorption not unconditionally valid for all photochemical systems. Finally, we shall meet a few theories in which the consequences of the quantum theory are not accepted at all.

Theories of Warburg and Nernst. Warburg's [7] and Nernst's [8] concept of the primary photochemical process is a dissociation of

[7] *Sitzb. Preuss. Akad.*, from 1913 to 1919, also *Z. Elektrochem.*, 27, 133 (1921).
[8] *Z. Elektrochem.*, 24, 335 (1919).

molecules on absorption of an energy quantum. The reactions of the free atoms produced are supposed to be the cause of deviations from the equivalence law. Discussing possible reactions of the atoms primarily formed, Warburg suggested that a reaction of the general type $A + B_2 \longrightarrow AB + B$ could occur only if the condition was fulfilled:

$$\log \frac{P_A \times P_{B_2}}{P_B \times P_{AB}} > \log K.$$

Here K is the equilibrium constant of the reaction $A + B_2 \rightleftarrows AB + B$, which can be calculated by means of the third law of thermodynamics, for instance by the approximation formula:

$$\log K = -\frac{Q}{4.57T} + \Sigma nC$$

where Q is the heat of the reaction $(A + B_2)$ and ΣnC the algebraic summation of the chemical constants of the components. Warburg's suggestion implies the assumption that the reactions of single atoms and molecules occur only when they are accompanied by a decrease in the free energy content of the reacting system.

Nernst pointed out that, when not only the reaction $A + B_2 \longrightarrow AB + B$, but also the subsequent reaction $B + A_2 \longrightarrow AB + A$ is thermodynamically possible, the atoms A will be continually regenerated by the second reaction and, therefore, a large number of reacting molecules per absorbed energy quantum will result.

Warburg stressed the point that the suggested primary process can occur only if the quantum energy of the absorbed radiation is larger than the heat of dissociation of the molecules. Quantum energy being smaller, no dissociation will take place and activated molecules must be formed. These can react only on collisions and only in such a way that the (negative) heat of the resulting chemical change is smaller than the quantum energy of absorbed radiation. Warburg suggested that, in photochemical reactions of this last type, smaller quantum yields than theoretically calculated should be expected, since not all activated molecules will have the opportunity to react.

The Stern-Volmer Theory of the Primary Process. Another concept of the primary process was put forward by Stern and Volmer.[9] They gave precision to the earlier theories of Luther ("activated" molecules), of Stark ("intramolecular photoelectric effect"), and suggested that, according to Bohr's theory, light absorption does not cause dissociation but excitation of molecules. A molecule is thus raised to a higher quantum state on absorption of a light quantum.

[9] *Z. wiss. Phot.*, 19, 275 (1920).

The excited molecules possess, according to Stern and Volmer, a high reaction ability and will undergo a chemical reaction on collision with some suitable (non-excited) molecule present in the reacting system.

Another process which can take place in excited molecules is the re-emission of light energy and this, together with the third possibility discussed below, must account for the cases in which the quantum yield of several photochemical reactions is too small. The third possibility for the excited molecules, as suggested by Stern and Volmer, is the loss of excitation energy by inelastic collisions with inert gas molecules. Since diatomic, and particularly, polyatomic molecules possess a large multiplicity of quantum levels, the loss of excitation energy will occur, in general, in small steps and, in this way, the absorbed light energy will be gradually dissipated and transformed into heat energy.

Drawing a parallel between the known phenomena of extinction of the fluorescence of iodine and mercury vapours by various added gases and the dissipation of excitation energy in photochemical processes, Stern and Volmer suggested that the excited molecules lose their energy more readily on collisions with molecules of electronegative than with those of electropositive gases. In the opinion of the authors, this suggestion accounts for the known specific retarding effect of oxygen and some other gases on the rate of certain photochemical reactions. Stern and Volmer criticized the Warburg-Nernst theory of primary dissociation of molecules and pointed to the observations on the spectrum of iodine vapour, from which it is known that iodine molecules remain undissociated even on absorption of light energy quanta larger than the heat of dissociation. This observation, in the opinion of the authors, is a direct proof of the correctness of their general theory.

The concept of activated molecules was already used by Bodenstein (previous to the publication of Stern and Volmer) for the explanation of the chain mechanism of the hydrogen-chlorine reaction. Later, Christiansen and Kramers [10] suggested that chain reactions caused by activated molecules are a general phenomenon and are not restricted to photochemical processes. According to their view, the products of a reaction of activated molecules must possess a large surplus of energy equal to:

$$A = h\nu + q + \tfrac{1}{2} mv^2$$

The first term in this equation is the absorbed radiation energy, which

[10] *Z. physik. C* ... **103**, 91 (1922); **104**, 451 (1923).

started the reaction, the second is the heat of reaction and the third is the kinetic energy (previous to reaction) of the reactants. This excess energy is transmitted by the products of reaction to other molecules of the reactant and, in this way, the activated molecules are continuously regenerated. The distribution of the excess energy among the different degrees of freedom of a molecule was not specified by Christiansen and Kramers. They suggested, however, that at least part of the energy is present in the form of kinetic energy of translational motion, and that activated molecules are "hot" molecules. Contradicting this last suggestion is the known absence of retarding action on the part of inert gases in many reactions, but Christiansen and Kramers postulate that the transfer of even the kinetic energy from molecule to molecule on collisions is specific in its nature.

The Primary Process according to Franck. Recently, Franck [11] has applied the results of the researches on molecular spectra to the discussion of the nature of the primary photochemical process. Franck points out that, according to the quantum theory of light absorption, the immediate result of light absorption is the formation of an excited molecule, but that, secondarily, an excited molecule can undergo a dissociation, even without the interference of collisions. Such dissociation in one elementary act is designated by Franck as adiabatic dissociation, and ... discusses the conditions necessary for such a process to take place.

Absorption of light by homopolar molecules results always in an increase of the energy of their electronic system, coupled with a change of the oscillatory energy of the atoms. It may be that the binding forces between the atoms are weakened by the increase of the electronic energy of the molecule. In such a case, suggests Franck, absorption of light causes an increase of the oscillatory energy and the molecule can undergo an adiabatic dissociation, provided, of course, the energy of absorbed radiation is large enough for this process. Of the resulting atoms, one will be in the normal quantum state; the other, however, will be excited, due to the fact that also in the molecule, prior to dissociation, one of the electrons was raised to a higher quantum state. If, on the other hand, the binding forces between the atoms are unchanged or strengthened by the electronic excitation within the molecule, there is little probability that such molecules will be adiabatically dissociated on light absorption. Franck's views on the intramolecular processes following light absorption can be best illustrated by the following diagrams (Fig. 1)

[11] *Trans. Farad. Soc.*, **21**, 536 (1925).

on which the potential energy of atomic oscillations E is represented as a function of the relative distance of the atoms d. Fig. 1a represents the state of a normal molecule prior to light absorption, the atoms oscillating with small amplitude (a) around the equilibrium position d_1. The change of electronic configuration on absorption of a light energy quantum, resulting in a change of the binding forces, will increase the equilibrium distance (to d'_1, see Fig. 1b) in case the

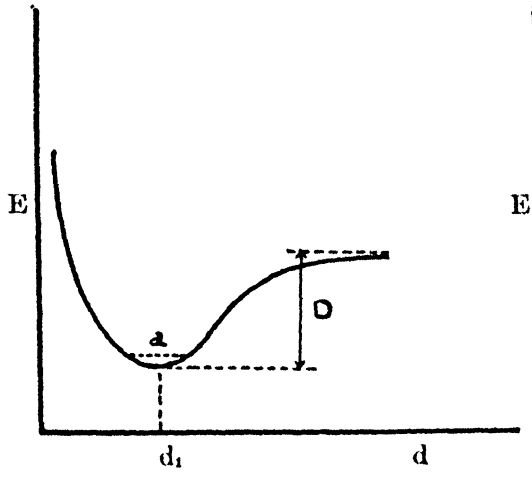


FIGURE 1a.

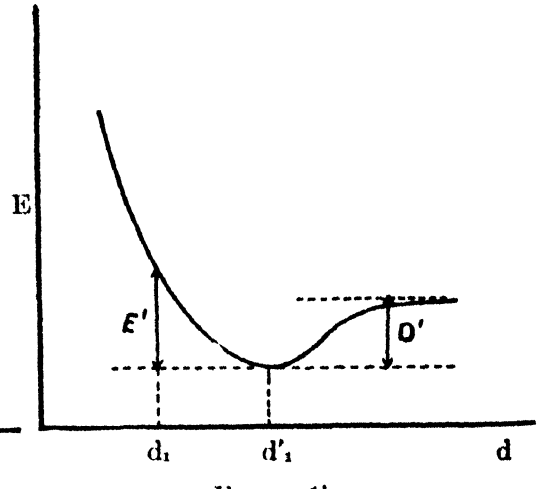


FIGURE 1b.

binding force has been weakened. During this process the atoms will have (on account of their slow motion) no opportunity to change their position and will be still at an average distance d_1. Their potential energy therefore will be increased (by E') and, provided this energy increase is larger than the energy of binding of the excited molecule (D'), the atoms will fly apart; that is, a dissociation will take place, within a time interval comparable to the time of one oscillation.

The relation of the strength of the molecular binding to the excitation of the atoms can be deduced from observations on the absorption spectra of molecules. Franck suggests that the halogen molecules belong to the type first described, whereas such unstable compounds as the mercury molecule Hg_2, which is formed only on collisions of excited mercury atoms with normal atoms, belong to the third type. Franck considered it, at the time of his first publication, as probable, that we have examples of the second type in such molecules as those of oxygen and nitrogen.

Discussing the processes following light absorption by heteropolar molecules, Franck pointed out that, in these, changes in oscillatory quantum energy can occur, as is evidenced by their absorption spectra,

independently of the change in the electronic system. Franck further arrives at the conclusion that, if an adiabatic dissociation of heteropolar molecules does occur, then ions must be formed and not atoms, since the ions and not the atoms are the oscillating parts of the molecule.

The Views of Weigert. Starting with an early paper,[12] Weigert has developed and modified in a series of publications a theory of photochemical processes, in which a sharp distinction is drawn between ideal photochemical reactions and real reactions. The equivalence law is strictly valid only for ideal processes and the deviations of the real ones are due not so much to the secondary reactions (of Bodenstein's type) as to the fact, normally ignored, that the whole Bohr concept of light absorption is strictly valid only for atoms and molecules at infinite dilution. In real photochemical reactions we deal usually with concentrated systems and here the mutual influences of neighboring molecules play an unknown but important rôle. The deviations from Beer's absorption law, frequently observed, are only an indication of this effect.

Weigert assumes that in gases, and more so in solutions, certain "clusters" of optically coupled molecules are usually formed. This process can change even the normal absorption spectrum of a substance. The absorbed light quantum energy will now be distributed among all components of the cluster and the amount available for a chemical reaction thus diminished. Weigert suggests further that the size of the optical "clusters," which determines the rate of a photochemical reaction, decreases with decreasing temperature, concentration and wave length of absorbed radiation. In more recent papers,[13] Weigert interprets the primary process, on light absorption, as an inner photoelectric effect and an intermediate formation of ions within the optical "clusters." The energy required to ionise a gaseous molecule is greatly diminished by the presence of dipole molecules in the "clusters" and other (electronegative) molecules acting as electron receivers.

Baly's Theory. Baly [14] postulated a specific form of quantum theory in which the free atoms are assumed to possess characteristic emission and absorption frequencies situated in the infra-red part of the spectrum. These frequencies are not changed if the atoms combine to molecules. The products of a photochemical reaction are further assumed to emit radiations of these frequencies, specific for the atoms

[12] *Z. Elektrochem.*, 14, 591 (1908); also, 23, 357 (1917).
[13] *Z. physik. Chem.*, 102, 416 (1922); 106, 426 (1923).
[14] *Rec. trav. chim.*, 41, 514 (1922).

forming the molecules, and the same frequencies are assumed to be reabsorbed by the reacting molecules, since they are composed of identical atoms.

In this way Baly explains the formation of a chain of reactions, caused by the excitation of a single molecule on light absorption. Baly further deduces that the rate of photochemical reactions must increase more rapidly than the intensity of the incident light.

Miscellaneous Theories. Though the quantum theory and its photochemical consequences seem to be becoming the basis of a steadily increasing amount of theoretical and experimental work on photochemistry, we find even now several theories based upon different concepts of the action of light energy. Lasareff [15] and Plotnikoff [16] suggest that, in general, a light sensitive substance possesses several light absorption bands of which only a part is photochemically active. The photochemical activity within each band is assumed to be proportional to the amount of absorbed light energy independent of the wave length, but the effect of different bands can be different. Lasareff suggests that the proportionality of a reaction rate to the expression $I_0(-c^{-acx})$ i.e., to the amount of absorbed light energy, is the fundamental law of photochemistry.

Plotnikoff developed mathematical expressions for the rate of different ideal photochemical reactions. It is a characteristic of his theory that the mass action law is applied not to the partial processes, as for instance by Bodenstein, but to the integral rate of reactions.

We have considered here in a somewhat abstract form a selection of modern theories on the kinetics of photochemical reactions. The reader will find in the following chapters these theories applied to the experimental material and will find also in the presentation of this same material a detailed discussion of these theories. Our survey is by no means complete. Some of the modern theories were intended to have only a limited application and they will be discussed in the following chapters as such. Other theories finally appeared to the writer to be of such an abstract character that no successful application in the treatment of photochemical kinetics could be expected. They are omitted from this survey.

[15] *J. chim. phys.*, 21, 161 (1923).
Trans. Farad. Soc., 21, 475 (1925).
[16] "Lehrbuch der Photochemie," Berlin, 1920.

CHAPTER II

THE EQUIVALENCE LAW

As has been already pointed out, the idea that light is absorbed by photochemically active molecules in definite energy quanta seems to be now almost generally accepted as the basis for the interpretation of the kinetics of photochemical reaction. Opinions on the nature of the primary and secondary processes are, however, widely varying and, though many of the theories described found a successful application in the treatment of the experimental material, it would be an impossible task to point out at present a theory that will account for all the experimental data.

Among the large variety of recently investigated and reinvestigated photochemical reactions, a certain rather limited number appears, from the point of view of quantum absorption, to offer less difficulties in the quantitative explanation of reaction kinetics. These reactions are usually classified as reactions following the equivalence law and they will be the chief object of consideration in the present section.

Assumptions made in the derivation of the equivalence law require that the rate of a photochemical reaction shall be independent of the concentration of the molecules present and of the temperature of the reacting body; the rate must be fully determined by the amount of absorbed light energy. Furthermore, one gram mol of the light absorbing component must react on absorption of an amount of light energy equal to $Nh\nu$. Thus, the rate of reaction per unit (calorie) of absorbed energy must depend on the wave length of active radiation. We find [1] that $\lambda \times 3.512 \times 10^{-9}$ gram mols of a substance must react according to the equivalence law on absorption of one calorie of light energy of the wave length λ. This relation shows that, with shorter wave length, the efficiency per gram calorie of radiation energy should decrease.

Warburg's Experimental Researches. Among the first who undertook the experimental verification of the equivalence law was Warburg. His extensive researches include a large variety of photochemi-

[1] λ, the wave length, is expressed in Angstrom units (Å.).

cal reactions, both in the gaseous phase and in solutions. His work undoubtedly must be considered as classical with regard to experimental skill and thorough theoretical treatment of the subject.

The results obtained by Warburg were in general not very favorable to a strict application of the equivalence law, but two of the reactions studied proved to be in relatively close agreement with the theoretical predictions of Einstein. These are the decompositions of gaseous hydrogen iodide and bromide.

Hydrogen-Iodide Decomposition. This reaction was discovered in 1877 by Lemoine and later studied by Bodenstein,[2] who used sunlight as the source of illumination and found a unimolecular reaction. The absorption spectrum of hydrogen iodide and its decomposition under the action of ultra-violet light were then studied by Coehn and Stuckard.[3] The absorption starts, according to these authors, at about 3300Å. and increases for shorter wave lengths. The decomposition under the action of light of wave lengths longer than 2500Å. is complete and only light of shorter wave length causes a partial formation of hydrogen iodide at about 270° C., the temperature of their experiments. Warburg [4] studied the reaction at room temperature and used monochromatic light of three different wave lengths as the source of illumination. The amount of absorbed light energy varied in these experiments in the ratio 1:2.2 and the partial pressure of hydrogen iodide, which was mixed with hydrogen, varied from 80 to 244 mm. The rate of reaction was found to be dependent only on the amount of absorbed light energy; Table 2 represents Warburg's results in a summarised form.

TABLE 2.

Wave length		2070Å.	2530Å.	2820Å.
$\frac{\text{Mols decomposed}}{\text{Calories absorbed}} \times 10^3$	found	1.447(±0.05)	1.85(±0.06)	2.08(±0.13)
	calculated [1]	0.73	0.89	0.993
	ratio	1.97±0.08	2.08±0.07	2.09±0.13

[1] From the equation on page 26.

These results indicate that, on absorption of one quantum of light energy, independent of its wave length, two molecules of hydrogen iodide are decomposed.

Recently Bodenstein and Lieneweg [5] extended the experiments of Warburg and measured the rate of reaction under widely varying

[2] *Z. physik. Chem.*, **22**, 23 (1897).
[3] *Ibid.*, **91**, 722 (1916).
[4] *Sitzb. Preuss. Akad.*, 300 (1918).
[5] *Z. physik. Chem.*, **119**, 123 (1926).

conditions. They found that an increase in temperature from 150° to 175° left the rate of reaction unchanged. Nitrogen also was without influence even at a pressure of 3.5 atmospheres. In presence of iodine, the rate of reaction is not accelerated, but retarded, this effect being due to the absorption of active radiation by iodine. Even liquid hydrogen iodide decomposes at room temperature at the rate of two molecules per absorbed light quantum.

Discussing the possible explanation of the observed quantum yield of two molecules, Warburg suggested that hydrogen iodide is decomposed into atoms on absorption of quantum energy of the active radiation. Warburg further suggested that the atoms formed could react in one of the following ways:

1. $H + HI \rightarrow H_2 + I$
2. $I + HI \rightarrow I_2 + H$
3. $H + H \rightarrow H_2$
4. $H + I \rightarrow HI$
5. $I + I \rightarrow I_2$

However, not all these reactions are equally probable. Warburg calculated the thermodynamic possibility of the first two by means of the equation mentioned on page 20. The first reaction, in the opinion of Warburg, occurs only if

$$(1)\quad \log \frac{p_H \times p_{HI}}{p_{H_2} \times p_I} > \log K;$$

Now, (2) $\log K = -\frac{Q}{4.57T} + \Sigma \nu C$; (3) $Q = -q_{HI} + q_{H_2}$

(4) $q_{HI} = \frac{1}{2}(Q_{2HI} + q_{I_2} + q_{H_2}) = \frac{1}{2}(2830 + 36300 + 100000) = 69600$ cal.

Therefore, (5) $Q = -69600 + 100000 = 30400$.

(6) $\Sigma \nu C = C_H + C_{HI} - C_{H_2} - C_I = 1.4$

Finally, we obtain:

$$(7)\quad \log K = -\frac{30400}{4.57T} - 1.4 = -24.2$$

Warburg assumed that the concentrations of the hydrogen and iodine atoms are equal; the ratio $\frac{p_{HI}}{p_{H_2}}$ was never less than 0.079. It follows that equation (1) is fulfilled and that therefore reaction (1) may be considered as possible. An analogous calculation for the second reaction shows its thermodynamic impossibility, so that the liberated iodine atoms can react evidently only by 5. The probability of reactions 3 and 4 is very small since the concentrations of the atoms are very low. The final result is that two hydrogen iodide molecules must be decomposed per absorbed quantum and this conclusion is in good agreement with what was observed by Warburg. Nernst and

Noddack [6] later criticised the application of thermodynamic equations as a guide to the reactions which actually take place among several possible reactions. They pointed out that thermodynamics can predict only the possibility of a reaction, but not its actual happening. Another objection is that if only reactions 1 and 5 take place, then, contrary to Warburg's assumption, the concentrations of iodine and of hydrogen atoms will be very different,[7] unless reaction 1 is very slow; this is highly improbable on account of experiments on hydrogen bromide formation to be discussed later. The unknown ratio of hydrogen and iodine atom concentrations will, of course, render the calculation of the logarithm of the concentrations uncertain.

Stern and Volmer reach identical results with respect to the quantum yield on the basis of their general theory of activated molecules as primary products of light absorption. They represent the reaction mechanism by the following sequence of reactions, in which HI′ refers to an activated molecule:

$$HI + h\nu = HI'$$
$$HI' + HI = H_2 + I_2$$

the quantum yield thus being also two. The inefficiency of hydrogen and nitrogen in retarding the rate of reaction is explained by Stern and Volmer as due to the fact that practically all collisions of the activated molecules with these electropositive gases are elastic, i.e., are not followed by the loss of activation energy. However, at very low concentrations of hydrogen iodide, when the life (or the average time between the absorption and re-emission of light) of activated molecules is comparable with the time between collisions of two hydrogen iodide molecules, a slowing down of the reaction rate should be observed.

Quite recently the study of the absorption spectrum of hydrogen iodide by Tingey and Gehrke [8] and by Bonhoeffer and Steiner [9] has apparently made possible a decision between the theories of Warburg and of Stern and Volmer. The absorption spectrum of hydrogen iodide was found to be entirely continuous and no traces of band structure could be observed in the wide spectral region studied (3320-2000 Å.). This observation, when interpreted on the basis of the quantum theory of molecular absorption spectra, indicates that the process following the absorption of light is a dissociation of the hydro-

[6] *Sitzb. Preuss. Akad.*, 110 (1923).
[7] According to modern theories, reaction 5 does not take place on every collision of two iodine atoms. Compare Born and Franck, *Z. Physik.*, 31, 411 (1925).
[8] *J. Am. Chem. Soc.*, 48, 1838 (1926).
[9] *Z. physik. Chem.*, 122, 287 (1926).

gen iodide molecule. According to Knipping,[10] no ions are produced on illumination of hydrogen iodide and, therefore, it must be concluded that this heteropolar molecule is dissociated into atoms. Franck [11] considered this process to be impossible in heteropolar molecules, but now, besides the study of the absorption spectrum of hydrogen iodide, other strong, although indirect, evidence supports Warburg's view of the reaction mechanism. To this we shall return later.

Hydrogen Bromide Decomposition. The decomposition of hydrogen bromide was first studied in some detail by Coehn and Stuckard.[12] Their experiments, carried out at 270° C. in the light of a mercury lamp, demonstrated that light transmitted by quartz causes a quantitative decomposition of hydrogen bromide. This reaction was later studied by Warburg [13] who, as in his studies on hydrogen iodide decomposition, used fairly monochromatic light and measured the light energy absorbed. For his experiments, carried out at room temperature, Warburg used mixtures of hydrogen and hydrogen bromide at atmospheric pressure. The partial pressure of the bromide was varied from 20 to 324 mm.; light intensity was varied in different experiments in the ratio 1:3.7. Because the light absorption of hydrogen bromide becomes too weak for wave lengths higher than 2600 Å., Warburg was forced to limit his experiments to two spectral regions of the mean wave lengths 2090 and 2530 Å. As in the case of hydrogen iodide, the rate of hydrogen bromide decomposition in each of these wave length regions was found to be entirely determined by the amount of absorbed light energy and to be independent of other variables. Also, the quantum yield was again found to be equal to two molecules, as the following table shows.

TABLE 3.

Wave length			2090Å.	2530Å.
Mols decomposed / Calories absorbed	$\times 10^5$	found	1.53 ± 0.08	1.79 ± 0.15
		calcul.	0.735	0.891
		ratio	2.08	2.01

Warburg discussed this reaction as already outlined in the case of hydrogen iodide and suggested the following mechanism:

$$1.\ HBr + h\nu \rightarrow H + Br$$
$$2.\ H + HBr \rightarrow H_2 + Br$$
$$3.\ Br + Br \rightarrow Br_2$$

[10] *Z. Physik*, 7, 328 (1921).
[11] *Loc. cit.*, p. 23.
[12] *Z. physik. Chem.*, 91, 722 (1916).
[13] *Sitzb. Preuss. Akad.*, 314 (1916).

The result of thermodynamic calculations exclude, in the opinion of Warburg, the possibility of the reaction:

$$4.\ Br + HBr \rightarrow Br_2 + H.$$

The reactions

$$5.\ H + H \rightarrow H_2$$
$$6.\ H + Br \rightarrow HBr$$

are improbable on account of the low concentration of hydrogen atoms. Stern and Volmer preferred to explain the reaction kinetics by assuming a formation of excited hydrogen bromide molecules and their subsequent reaction on collision, but Tingey and Gehrke [14] found no indication of absorption bands in the continuous absorption spectrum of hydrogen bromide and therefore favored the mechanism advanced by Warburg.✓

Dissociation of Alkali Halides. Investigation of the action of light on vapours of different alkali halides have been initiated only in recent years; but, already, they have led to results of quite general importance in the treatment of photochemical kinetics, and, in particular, in the interpretation of the hydrogen iodide and bromide decompositions. Terenin [15] was the first to notice that sodium iodide vapour, at low pressures, emits the first sodium resonance (*D*) lines when illuminated by light of shorter wave length than 2500Å. Under illumination by wave lengths 1844-1862 Å., the second resonance lines of sodium (3306-3302 Å.) also appear in the fluorescence spectrum. Similarly, Kondratjeff [16] found that caesium iodide vapour emits the second resonance line (4556 Å.) of caesium, when illuminated by light of the wave lengths 1844-1862 Å. On the other hand, no visible fluorescence is emitted on absorption of light of the wave length region around 2300 Å., the experiments being incapable of detecting the first resonance line of caesium since it is situated in the infra red spectral region. Kondratjeff also demonstrated that the life of activated sodium iodide molecules—assuming that such are formed on light absorption—is short in comparison with the average time between molecular collision in the pressure range investigated (10^{-3} — 10^{-2} mm.); and, that the intensity of sodium fluorescence is proportional to the amount of absorbed light energy, being independent of the collision frequency. These spectroscopic and kinetic observations led him to the conclusion that alkali iodides are dissociated into a normal iodine atom and an excited alkali atom on absorption of light energy and that this process directly follows the process of light absorption

[14] *Loc. cit.*
[15] *Z. Physik*, 37, 98 (1926).
[16] *Ibid.*, 39, 191 (1926).

without the intervention of secondary molecular collisions. Furthermore, the wave length of the absorbed radiation determines the quantum state of the excited alkali atom according to the energy relation:

$$h\nu \geqq \text{Energy of dissociation} + \text{Energy of excitation.}$$

The objection might be raised that this interpretation of the experimental results is in complete disagreement with Franck's conclusion as to the impossibility of dissociation of polar, ionically bound, molecules into atoms on light absorption, discussed in the first section of this book. However, the latter's conclusions have been obviated by Hund,[17] who has shown theoretically that light absorption by ionically bound polar molecules may lead to the shift of the valence electron from the anion to the cation; with the result that, if sufficient oscillation quantum energy is supplied and dissociation of the molecule takes place, neutral atoms, not ions, are produced. Furthermore, in contradistinction to the behaviour of homopolar molecules, which will dissociate only when the energy of the absorbed light is sufficiently high to produce one excited and one normal atom, in the case of ionically bound molecules dissociation will occur even when the energy supplied by absorption of light is so low that two normal atoms are formed. This last conclusion has recently been tested by Franck, Kuhn and Rollefson.[18] Extending the earlier investigations of Angerer and Müller[19] and of Müller,[20] they studied the absorption spectra of alkali halide vapours; and found them wholly continuous, without any indications of a band structure. In the spectral region investigated (4000-2300 Å.), the chlorides were found to have one absorption maximum; bromides, two; and iodides, two and a beginning of a third extending to shorter wave lengths. The authors assumed that those continuous bands which are situated on the long wave length side of the absorption spectra, correspond to the dissociations of the molecules into two normal atoms. The second bands indicate the occurrence of dissociation into an excited halogen and a normal alkali atom, since excitation of alkali atoms would require considerably more energy and the corresponding bands should lie in the shorter ultraviolet, as indicated by the presence of the third band in the spectra of iodides and particularly as shown by the experiments of Terenin and of Kondratjeff previously discussed. Table 4 summarizes the data of Franck and his co-workers, of Terenin and of Kondratjeff on the energy changes involved in the processes occurring. In the

[17] *Z. Physik*, 40, 742 (1927).
[18] *Ibid.*, 43, 155 (1927).
[19] *Ibid.*, 26, 643 (1925).
[20] *Ann. Physik*, 82, 39 (1927).

second column is the process occurring on light absorption, the excitation of an atom being denoted by an asterisk; in the third, the long wave length side of the corresponding band in Å. units and the $Nh\nu$ values in cal; while in the fourth, under $N(h\nu_2\text{-}h\nu_1)$, the energy difference between the absorption maxima of the first and of the second alkali halide bands in the experiments of Franck and co-workers, which should be approximately equal to the excitation energy of the halogen atoms; in the fifth column, the atomic excitation energies calculated from spectroscopic data; and, finally, the last two columns furnish a comparison between the heats of dissociation of alkali halides into normal atoms as calculated from these experiments by means of the equation on page 32, and as determined from thermochemical data.

TABLE 4.

1	2	3 Å.	3 $Nh\nu$	4 $N(h\nu_2 - h\nu_1)$	5	6	7
			cal	cal	cal	cal	cal
	Na+I	>3900;	<73,000			<73,000	63,000
NaI	Na+I*			*22,600*	$2^2P_2-2^2P_1=21,500$		
	Na*+I	2500;	114,000		1S−2P=48,000	65,000	63,000
	Na*+I	>1862;	<153,000		1S−3P=86,000	67,000	63,000
CsI	Cs+I	3800;	75,000			75,000	75,000
	Cs*+I	>1862;	<153,000		1S−3P=62,400	<90,000	75,000
KI	K+I	3800;	75,000			75,000	84,000
NaBr	Na+Br	3100;	91,000			91,000	84,000
	Na+Br*			*9300*	$2^2P_2-2^2P_1=10,400$		
KBr	K+Br	3100;	91,000			91,000	100,000
	K+Br*			*8500*	$2^2P_2-2^2P_1=10,400$		
RbBr	Rb+Br*			*8700*	$2^2P_2-2^2P_1=10,400$		
NaCl	Na+Cl	2800;	103,000		$2^2P_2-2^2P_1=2,500$	103,000	103,000
	Na+Cl*			*0*			

The agreement of these figures (columns 4 and 5, and 6 and 7 respectively), is, on the whole, more than satisfactory, particularly when it is considered that the limit or the maximum of a continuous absorption cannot be determined with that precision usually attainable in determinations of a spectral line or of a band convergence limit. These energy calculations thus fully support the theory advanced. Further evidence may be obtained from the qualitative experiments of Hogness and Franck,[21] who showed that, with increasing energy of absorbed quanta, the alkali fluorescence lines become more diffuse, due to increasing Doppler effect. This is interpreted as an indication that the surplus energy of the quantum absorbed by the molecule is transformed into kinetic energy of the atoms flying apart.

[21] *Z. Physik*, **44**, 26 (1927).

On the other hand, this simple relation between the long wave length limit of the absorption spectra of alkali halides and their heats of dissociation, does not exist in the case of hydrogen halides. It is possible to calculate the heats of dissociation of the latter with considerable precision owing to the knowledge of the exact values for the heats of dissociation of hydrogen and of halogen molecules:

$$H_2 \rightarrow 2H - 101{,}000 \text{cal.}^{22}$$
$$I_2 \rightarrow 2I - 35{,}200 \text{ cal.}^{23}$$
$$Br_2 \rightarrow 2Br - 45.200 \text{ cal.}^{23}$$

It follows: [24]

$$HI \rightarrow H + I - 69{,}000 \text{ cal.}$$
$$HBr \rightarrow H + Br - 85{,}000 \text{ cal.}$$

whereas the continuous absorption of hydrogen iodide ceases at 3200 Å. ($Nh\nu = 89{,}000$ cal.), and that of hydrogen bromide between 2600 and 2800 Å. ($Nh\nu = 109{,}000$-$101{,}000$ cal.). Franck and Kuhn [25] found similar disagreement in the case of vapours of silver bromide and iodide, the limits of their continuous spectra indicating much higher heats of dissociation than determined thermochemically. To avoid the resulting difficulty, the authors suggested that these molecules, although polar, are not composed of ions, but of atoms. They find their suggestion supported in certain investigations involving the electrical and optical properties of silver halides in the solid and molten states, a discussion of which, however, cannot be undertaken here. As has been pointed out (see first chapter) molecules of which atoms and not ions are the oscillating parts can be dissociated on light absorption only if one (or both) of the atoms produced is in an excited state. Franck and Kuhn assume, therefore, that silver halides are dissociated into a normal silver atom [26] and an excited halogen atom, and, calculating the energy changes involved, arrive at a more satisfactory agreement with thermochemical data. They apply the same mechanism to the case of the hydrogen halides, suggesting that the nature of the binding is the same (atomic) type, and that therefore they, also, can be dissociated only if an excited halogen atom is produced. The data on hydrogen iodide fully confirm their view:

$$Nh\nu_{\text{abs.}} - Nh\nu_{\text{excit.}} = Q_{\text{diss.}} = 89{,}000 - 21{,}500 = 67{,}500 \text{ cal.}$$

instead of 69,000 cal. In the case of hydrogen bromide the agreement is less satisfactory

$$109{,}000 - 10{,}400 = 98{,}600 \text{ cal.},$$

[22] Dieke and Hopfield, *Z. Physik*, **40**, 299 (1926).
[23] Kuhn, *Z. Physik*, **39**, 77 (1927).
[24] Comp. Landolt-Börnstein Tabellen.
[25] *Z. Physik*, **43**, 164; **44**, 607 (1927).
[26] Excitation of the silver atom in this spectral region is out of the question since

instead of the 85,000 cal. calculated from thermochemical data; but this discrepancy is possibly due to the uncertainty of the absorption limit of hydrogen bromide.

Nernst's Researches on the Equivalence Law. With the idea that the primary action of light on halogens was their dissociation into atoms, Nernst suggested that, with suitable atom "acceptors" present in the system, the atoms formed would react quantitatively, yielding two molecules of the reaction product per quantum. In his laboratory, several reactions of this type were therefore studied. Pusch,[27] investigating photosensitive mixtures of bromine and toluene, heptane, hexane and hexahydrobenzene vapours, found only in the last reaction an approximate conformity with the theory, other reactions being too fast (up to 20 molecules of bromine reacting per absorbed quantum) and proceeding in the dark after illumination. Noddack [28] confirmed the results of Pusch for the bromine-hexahydrobenzene reaction that one molecule of bromine reacts per absorbed light energy quantum. The light used in his experiments, as also in those of Pusch, was not monochromatic, since the region 4400-5300 Å. was isolated by means of light filters and the absorbed quanta were calculated for the mean wave length 4690 Å. The products of reaction were not studied, only the rate of disappearance of bromine being measured. The mechanism of this bromination may thus be uncertain. Noddack,[29] and later Grüss,[30] studied the rate of chlorination of CCl_3Br by dissolved chlorine under the action of light absorbed by the latter. The rate of reaction in pure CCl_3Br as measured by Noddack corresponded to one molecule of chlorine reacting per absorbed quantum. Two types of light filters were used, transmitting 4400-3910 Å. and 4680-4400 Å., the number of quanta being calculated for 4100 Å. and 4490 Å. The admixture of carbon tetrachloride decreased the yield of reaction. Noddack suggested that activated chlorine molecules are formed by absorption of light energy and they are deactivated in dilute solutions before they collide with CCl_3Br to react according to the scheme:

$$\begin{aligned} (1)\ & CCl_3Br + Cl_2' = CCl_4 + Cl + Br \\ (2)\ & CCl_3Br + Cl = CCl_4 + Br \\ (3)\ & Br + Br = Br_2. \end{aligned}$$

Grüss showed, however, that using thoroughly purified carbon tetrachloride and silicon tetrachloride, the reaction proceeded at the rate

it would require considerably more energy than is available in the absorbed light quanta.

[27] *Z. Elektrochem.*, 24, 336 (1918).
[28] *Ibid.*, 27, 359 (1921).
[29] *Ibid.*
[30] *Z. Elektrochem.*, 29, 144 (1922).

of one molecule of chlorine per quantum, even in solutions containing only 1 part of CCl_3Br in 50 parts of silicon tetrachloride and in 80 parts of carbon tetrachloride, the retardation observed by Noddack being due to impurities. To reconcile this fact with the treatment of the reaction mechanism given by Noddack, Grüss suggested that the life of excited chlorine molecules is of the order of 10^{-7} sec. and that almost all collisions with CCl_4 and $SiCl_4$ molecules are elastic. It must be noted, however, that the calculation of the mean life of excited molecules in liquid systems, which was based on the fact, that, in very dilute solutions of CCl_3Br in CCl_4 and $SiCl_4$, a decrease of the yield was observed, is very doubtful, since nothing definite is known about the mean free path and the number of molecular collisions in liquids. Further, the observed decrease of the yield might be due—as in the experiments of Noddack—to the last traces of impurities in the substances used. All things considered, nothing definite can be said as to the mechanism of this reaction, since the hypothesis of free atoms leads to the same yield of one molecule per quantum.

Decomposition of Chlorine Oxides. The gaseous reactions discussed so far were endothermic reactions and, as, on the other hand, many exothermic reactions show a marked deviation from the equivalence law, it seems to be of interest that at least in two cases we have exothermic gaseous reactions following the equivalence law closely. These are the decompositions of ozone in presence of chlorine and of gaseous chlorine monoxide. Both these reactions belong to the class of the so-called photosensitised reactions and will be discussed in a subsequent chapter. It suffices now to note that, in both cases, we have two molecules decomposed per quantum.

Bowen [31] studied the decomposition of chlorine monoxide and of chlorine dioxide dissolved in carbon tetrachloride under the action of blue light of wave length 4100-4700 Å. Both reactions proved to be dependent only on the amount of absorbed light energy, the concentration of the dioxide being varied from 0.32 to 0.035 mols per liter and that of the monoxide from 0.14 to 0.085 mols per liter. The light intensity was varied in the ratio 1:6. The absolute measurements of the absorbed light energy were not very exact, the inconstancy of the light source alone amounting to 25 per cent and a rather rough energy measuring system being employed. Calculating the number of quanta for the average wave length 4450 Å. Bowen found, for chlorine dioxide, the ratio 0.83 molecules per quantum and for chlorine mon-

[31] *J. Chem. Soc.*, 123, 1199 (1923).

oxide 0.90, or near enough to unity to suggest the ratio 1.0 in both cases.

Discussing the possible mechanism of these reactions, he suggested that the reactions proceeded in the way indicated by equations 1 and 2:

$$(1)\ ClO_2 \rightarrow Cl + O_2 - 10{,}000\ \text{cal.}$$
$$(2)\ Cl_2O \rightarrow Cl_2 + O - 64{,}000\ \text{cal.}$$

the energy of the quanta of blue light (equal to about 64,000 cal.) being too small for the following reactions:

$$(3)\ ClO_2 \rightarrow Cl + O + O - 170{,}000\ \text{cal.}$$
$$(4)\ Cl_2O \rightarrow Cl + Cl + O - 118{,}000\ \text{cal.}^{33}$$

The mechanism suggested is, however, highly improbable. The free chlorine atom in the one case and especially the oxygen atom in the second would undoubtedly react with molecules of chlorine oxides present, yielding finally two molecules per quantum. In the case of chlorine monoxide, the yield of two molecules in the gaseous phase was actually observed, as mentioned before, and explained, in good agreement with other observed facts, by the mechanism:

$$(1)\ Cl_2O + h\nu = Cl_2O'$$
$$(2)\ Cl_2O' + Cl_2O = 2Cl_2 + O_2$$

The reinvestigation of the reactions discussed and a study of possible by-products [33] seems to be desirable since the application of the above mechanism to the case of solutions of monoxide and dioxide leads also to a yield of 2 molecules per quantum.

Hydrolysis of Monochloracetic Acid. A recent study of the rate of hydrolysis of monochloracetic acid by Rudberg [34] also gave a value for the photochemical yield equal to unity. The reaction can be expressed by the equation:

$$ClCH_2COOH + H_2O = HOCH_2COOH + Cl^- + H^+$$

The rate is slow in the dark and is accelerated by the presence of hydroxyl ions. The photochemical reaction in ultraviolet light was first studied by Euler and Cassel,[35] who used the total radiation of a mercury lamp. The calculated unimolecular constants were found to increase with dilution, indicating a large but not complete absorption of active rays. The constants, however, decreased with time of illumination of a given solution, suggesting that the hydrochloric acid

[33] These heat values are calculated on the basis of more recent data on the heat of dissociation of chlorine (— 54,000 cal.) and that of chlorine dioxide (+ 34,000 cal. for $2ClO_2$: Meyer, Dissertation. Hanover, 1924). For chlorine monoxide, the value + 32,000 cal. and for oxygen, — 160,000 cal. were used.

[33] Bowen, however, remarks that no reaction with carbon tetrachloride could be observed (*loc. cit.*).

[34] *Z. Physik.* **24**, 247 (1924).

[35] *Z. physik. Chem.*, **84**, 371 (1913).

formed was retarding the rate of reaction. Rudberg used monochromatic light of wave length 2536 Å. and measured the absorbed energy. Correcting the values for absorption and reflection in glass and water, the yield of 1.05 molecules per quantum was obtained by him for 0.5 normal and a yield of 0.95 for 0.3 normal solutions of chloracetic acid in pure water. No experiments with added acids or bases were reported. Monobromacetic acid, which was also studied, showed a different behaviour. This hydrolysis proceeds in the dark at a measurable speed and the rate of photochemical reaction was obtained by subtracting the dark value from the total change observed. On account of much stronger light absorption than that of monochloracetic acid, more dilute solutions were used and values of 0.35 molecules per quantum for 0.02 N and 0.32 for 0.01 N were obtained. On addition of an equivalent amount of sodium hydroxide the yield was increased to 0.47; double the amount of hydroxide brought it to 0.54. Special experiments with sodium sulfate indicated that the increase in the photochemical yield is due to the presence of hydroxyl ions. Of course, the simplest assumption would be that only those molecules of monochloracetic acid are hydrolysed which, within a certain time after light absorption, collide with a hydroxyl ion. However, Rudberg calculates that, in this case, the quantum yield of the reaction would be represented by the equation $\varphi = 1 - e^{-z \cdot c}$, where z is the mean life of activated acid molecules and c the concentration of hydroxyl ions. According to this equation, the yield of the reaction should be equal to unity already in solutions containing only one equivalent of sodium hydroxide, so that the assumed reaction mechanism cannot be correct.

Euler [36] applied his general theory of homogeneous catalysis of hydrolytic reactions to the discussion of Rudberg's experimental data. This theory includes the intermediate formation of "reaction transmitting ions" and their photochemical activity, but the calculations of Euler do not explain the difference in the quantum yield of both cases of hydrolysis studied. If some attention be paid to the observed small decrease in the quantum yield with decreasing concentrations of both acids (which is, however, within experimental error according to Rudberg), then the question arises, whether or not in more dilute solutions of monochloracetic acid similar deviations from the quantum yield of unity would be observed and the conclusion could be made that both reactions are similar in character. Of course, the conformity of the monochloracetic acid hydrolysis to the equivalence

[36] *Z. physik. Chem.*, **110**, 243 (1923); *Z. Physik*, **16**, 54 (1923).

law must then be considered as somewhat accidental, until a further study of the reaction kinetics reveals the cause of deviations by demonstrating the presence of some secondary reactions. The decrease of the unimolecular constants with time of illumination, observed by Euler and Cassel, seems to support this view.

Oxidation of Quinine. An interesting, but not completely explained, photochemical reaction is the oxidation of quinine by chromic acid in presence of sulfuric acid. This reaction was studied by Goldberg,[37] who noticed a very small temperature coefficient (1.02). It was later the object of an extensive investigation by Luther and Forbes,[38] which revealed interesting relations.

Not only quinine, but also chromic acid, absorbs the light which is causing the photochemical reaction. Now, the light energy absorbed by a layer dx of the mixed solution of both substances is $-dI_{abs.} = I(a_1c_1 + a_2c_2)\,dx$ where $a_1;c_1;a_2;c_2$ are respectively light absorption coefficients and concentrations of both components. The fraction of light energy which is absorbed by quinine in the layer dx of the mixed solution is $-dI_{abs.quin.} = Ia_1c_1.dx$, and, since the ratio of both expressions,

$$(1)\quad \frac{dI_{abs.\,quin.}}{dI_{abs.}} = \frac{a_1c_1}{a_2c_2 + a_1c_1}$$

is independent of the layer thickness, this equation gives directly the fraction of the total absorbed energy which is absorbed by quinine.

Luther and Forbes measured the absorption coefficients (a) of both substances and demonstrated, by applying equation 1, that the light absorbed by chromic acid is ineffective; the latter is therefore acting only as an inner screen. The authors demonstrated, further, that the rate of reaction was proportional to the amount of light energy absorbed by quinine and was independent of the chromic acid concentration, at least when this latter was varied from 0.012 to 0.001 N. At still lower concentrations of chromic acid, a decrease in the rate of reaction was observed. The reaction was studied in monochromatic light and identical kinetic relations observed under the action of the mercury lines 4060 Å. and 3660 Å.

Recently, Forbes and co-workers [39] have extended the earlier experiments of Luther and Forbes and studied in particular the influence of sulfuric acid. They found that the rate of reaction is practically

[37] *Z. wiss. Phot.*, **4**, 56 (1906).
[38] *J. Am. Chem. Soc.*, 31, 770 (1909).
[39] *Ibid.*, **45**, 1891 (1923).

independent of the concentration of sulfuric acid,[40] only, however, if this is above 0.5 normal; in more dilute solutions, a decrease in the rate of oxidation approximately proportional to the concentration of the acid was observed. Calculating the efficiency of light energy in producing chemical reaction on the basis of the available data of Ladenburg [41] on the energy distribution in the mercury arc, Luther and Forbes came to the conclusion that the light of wave length 4060 Å. was four times more efficient (per absorbed calorie) than that of wave length 3660 Å. This last statement seems, however, to need reinvestigation as being unique and rather improbable. The possible absorption of the wave 3660 in the glass vessels used and possibly a different spectral distribution of energy in the uviol lamp, as compared with a quartz arc studied by Ladenburg would account for the astoundingly rapid increase in efficiency with increasing wave length (the equivalence law predicting only 11 per cent increase). The photochemical yield of this reaction was not directly measured. Bodenstein [42] calculated, on the basis of the data of Ladenburg, the approximate absolute energy absorbed by quinine in the experiments of Luther and Forbes and obtained the number 12.10^{17} quanta of the line 3660 Å. absorbed per second as compared with 8.10^{17} molecules of quinine being oxidised per second. Thus, at least an approximate validity of the quantum law is evident for this reaction. Discussing the possible reaction mechanism, Luther and Forbes suggested that, at higher chromic acid concentrations, the rate of reaction was determined by the speed of the primary process—the light absorption—and that, on the contrary, at low concentrations of the acid, the rate of reaction was determined by the rate of oxidation. In accordance with these suggestions Bodenstein (*loc. cit.*) proposed a mechanism, which, slightly modified, could be expressed as follows:

(1) Quinine + $h\nu$ = Q′ (activated molecule of quinine); k_1
(2) Q′ → Q (inactivation) ; k_2
(3) Q′ + CrO_3 → oxidation product ; k_3

The rate of single reactions is represented by the equations:

$$(4)\ +\frac{d[Q']}{dt} = k_1 I_{abs.} \qquad (5)\ -\frac{d[Q']}{dt} = k_2[Q'] + k_3[Q'][CrO_3]$$

The square brackets indicate here, as in all subsequent equations, the concentrations of reactants. Very soon after the illumination has been

[40] With the exception of an uncertain maximum at about 1.0 *N* which is not more than 10 per cent higher than the average.
[41] *Physik. Z.*, 5, 595 (1904).
[42] *Z. physik. Chem.*, 85, 329 (1913).

started, the rate of formation of activated molecules must become equal to the rate of their destruction, or

$$(6)\quad k_1 I_{abs.} = k_2 [Q'] + k_3 [Q'] [CrO_3].$$

Therefore

$$(7)\quad [Q'] = \frac{k_1 I_{abs.}}{k_2 + k_3 [CrO_3]}$$

Introducing this expression into equation (3) we obtain:

$$(8)\quad -\frac{d[CrO_3]}{dt} = k_3 [Q'] [CrO_3] = I_{abs.} \frac{k_1 k_3 [CrO_3]}{k_2 + k_3 [CrO_3]} = I_{abs.} \frac{k_1 [CrO_3]}{\frac{k_2}{k_3} + [CrO_3]}$$

A good agreement of this equation with the experimental results of Luther and Forbes can be obtained if the ratio $\frac{k_2}{k_3}$ be assumed equal to 0.0003 (Bodenstein).

TABLE 5.

⅓ $[CrO_3]$	0.0026;	0.0019;	0.0013;	0.0010;	0.0005;	0.00015;	0.00007 normal
$\frac{\Delta x}{\Delta t}$ meas.	1.11	1.31	1.33	1.01	0.87	0.50	0.26
$\frac{\Delta x}{\Delta t}$ calcul.	1.25	1.19	1.11	1.07	0.87	0.47	0.27

Bodenstein, suggesting the reaction mechanism discussed above, neglected to take into account the dependence of the reaction velocity on the acid concentration. Perhaps it is significant that sulfuric acid increases not only the oxidation velocity, but also the fluorescence ability of quinine. If it may be so expressed, sulfuric acid "stabilises" the activated molecules against the loss of energy on inelastic collisions, and, in this way, promotes either their reaction or the emission of fluorescence. It is uncertain at present whether this action should be attributed to the formation of a quinine acid complex possessing, in the excited state, a remarkable stability.

The Photosensitivity of Silver Halides. A photochemical reaction which found a very important technical application and which is the object of an unusually large number of investigations is the action of light on solid silver salts, notably the halides.

Since the time of Daguerre's first light sensitive plates the technique of photography has undergone a rapid process of development. Now, after ninety years of technical research, photographic plates for every scientific and artistic purpose are available; plates, the sensitivity and other characteristics of which, can be regulated at will by

the mode of preparation, and which can be made sensitive not only to all frequencies of the visible, but also to infra-red and to far ultra-violet sections of the spectrum. The theory of photography unfortunately did not entirely keep pace with its technical development, notwithstanding continuous and extensive research. Even the basic problem of photography, the nature of the photochemical reaction in the light sensitive emulsions, has been more or less definitively answered only in recent years. Theories of other important photographic factors, such as plate sensitivity, developer action, etc., are still essentially lacking. Here, however, we cannot enter into a discussion of these various problems; reference must be made to standard works on photography. In this section, only the mechanism of the photochemical reaction in silver halides and the relations of this photoaction to the equivalence law will be discussed, the problem of the photosensitisation of the photographic emulsions to different wave lengths being dealt with in one of the subsequent chapters.

Emulsions employed for the preparation of photographic plates and films,[43] consist of a colloidal suspension of silver halides—mainly silver bromide with a small amount of silver iodide—in gelatin. X-ray examinations[44] of these colloidal particles revealed that they have a crystalline structure of a type belonging to the regular system. The change in the photographic emulsions upon short illumination is invisible; it can be intensified, however, by the use of a suitable reducing agent, the exposed silver halide being reduced to colloidal silver but no reduction taking place in unexposed parts of the emulsion. In contrast to the action of developers, strong oxidising agents destroy the photoaction and prevent a subsequent development. A more extensive illumination causes a visible change in the silver halides manifested by their variable coloration. Pre-illuminated emulsions are sensitive to light of longer wave lengths than before the treatment. These and other properties of the "latent image" have found, since the discovery of photography, divers explanations in the many theories for the photochemical process. Depolymerisation,[45] mechanical disintegration,[46] polymerisation,[47] mechanical strain,[48] oxidation,[49] formation of a labile form,[50] formation of distinct subhalides ($Ag_n Hal_m$;

[43] Not of reproducing papers.
[44] Trivelli and Sheppard, "The Silver Bromide Grain." Monograph I. Eastman Kodak Lab., D. VanNostrand Company, 1921.
Wilsey, *Phil. Mag.*, 42, 262 (1921).
[45] Hurter and Driffield, *Photogr. J.*, 22, 149 (1898).
[46] Bredig, *Eder's Jahrbuch. Phot.*, 13, 365 (1899).
[47] Namias, *Chimie Photographique*, 102, 110 (1902).
[48] Bose, *Phot. J.*, 26, 146 (1902).
[49] Tugolessow, *Phot. Correspondenz*, 40, 594 (1903).
[50] Chapman Jones, "Science and Practice of Photography," 383 (1904).

n>m),[51] have all been proposed, but none of these suggestions have attracted more than a passing attention with the possible exception of the theory of subhalides. The latter was apparently substantiated by the previously mentioned observations on the colour changes of illuminated silver halides and the simultaneous extension of sensitivity to light of longer waves. Trivelli, for example, postulated the existence of green Ag_8Br_7, blue Ag_8Br_6, etc., assuming these subhalides to be developable and to be sensitive to longer waves than the original silver bromide. The theory of subhalides, however, lost considerable ground after Lüppo-Cramer [52] succeeded in showing that all effects attributed to "subhalides" could be reproduced by adding colloidal silver to the photographic emulsions. Furthermore, all attempts to isolate subhalides were fruitless.

The theory which now enjoys a more or less general recognition was originally suggested by Carey Lea [53] and later supported by Lüppo-Cramer.[54] It assumes that the substance of the latent image is silver adsorbed on silver halide. The experiments of Lüppo-Cramer mentioned above are undoubtedly a very strong evidence in favour of this suggestion, since they show that the latent image can be synthetically reproduced by allowing colloidal silver to be adsorbed on the halide particles of the emulsion. It would be useless to draw into the discussion all the experimental material which is available on the subject. It suffices to mention that Lorenz and Hiege [55] observed the formation of a metallic cloud in crystals of silver halides on illumination; and that recently, Hartung,[56] working with a micro-balance, demonstrated that thin films of silver halides lose weight on illumination, and that the weight can be restored by a subsequent halogenation. In vacuo, the reaction proceeds more rapidly and can be carried out almost quantitatively to the stage of pure silver.

Intimate knowledge of the processes taking place in photographic emulsions on illumination has been obtained by means of microscopic study carried out in recent times particularly by Svedberg,[57] by Slade and Higson,[58] by the Eastman Kodak Laboratory [59] and by

[51] Luther, *Z. physik. Chem.*, 30, 618 (1899); Trivelli, *Z. wiss. Phot.*, 6, 197, 237, 273 (1908); 8, 117 (1910); 9, 187 (1911).
[52] "Kolloidchemie und Photographie" (1908).
[53] *Am. J. Sci.*, 3, 33, 349 (1887).
[54] See "Kolloidchemie und Photographie" (1908).
[55] *Z. anorg. Chem.*, 92, 27 (1915).
[56] *J. Chem. Soc.*, 121, 682 (1922); 125, 2198 (1924); 129, 1349 (1926); see, for contradicting evidence: Koch and Schrader, *Z. Physik*, 6, 127 (1921).
[57] *Z. wiss. Phot.*, 20, 38 (1920); *Phot. J.*, 61, 325 (1921); 62, 180, 310 (1922).
[58] *Phot. J.*, 59, 260 (1919); 61, 35, 144 (1921); *Proc. Roy. Soc.*, 98A, 154 (1920).
[59] Trivelli, Righter and Sheppard, *Phot. J.*, 62, 407 (1922); *Sci. Pub. Eastman Kodak Res. Lab.*, 7, 84 (1924), etc.

others. The essential results of these investigations may be summarised as follows:

1. The action of light either does not change a grain in an emulsion at all, or makes it entirely developable; the developability is limited to the grain itself and is not transmitted to the neighbouring ones. Sometimes, however, a clump of grains may act as a unit.

2. The probability of a grain becoming developable on illumination is governed by the laws of chance. The sensitivity of all the grains, however, is not the same. Larger grains are more sensitive; but even grains of approximately the same size and shape can apparently differ in sensitivity. This is particularly true if grains from different emulsions are being compared.

3. The development of the grains starts from certain points—"the centres"—which are visible on the grain as dark spots if the development is interrupted before completion. Each grain which contains at least one centre is completely developable.

4. In a given size class of grains the distribution of centres after illumination is governed by the laws of chance. If the average number of centres per grain is ν, then the probability that a grain contains η centres is given by the equation:

$$\frac{e^{-\upsilon}\,\nu^{\eta}}{\eta\,!}$$

5. The number of centres increases with exposure.

6. The centres are located not only on the surface of the grains but also in their interior. This statement is substantiated by the experiments of Lüppo-Cramer on the "Keimblosslegung." Lüppo-Cramer demonstrated that the developability of an illuminated emulsion destroyed by an oxidising agent can be restored by dissolving the surface layer of the halide grains. (*Cf.* "Kolloidchemie und Photographie".)

7. Under normal conditions the development starts only from those centres which are situated on the surface of the grains. With spherical grains, these centres are distributed equally over the surface; but with flat grains, the usual shape of grains in technical emulsions, the centres are concentrated mostly on the edges of the flat plates.

If the attempt be made to co-ordinate the "macroscopic" theory of the latent image with the microscopic evidence for the existence of development centres in illuminated emulsions, the conclusion might be reached that these centres are adsorbed silver atoms or silver atom aggregates. Opinions as to the origin of the centres, however, differ.

Toy [60] and others suggested that the "centres" exist in the grains prior to illumination and that the action of light consists solely in making them active for the development process. The experimental fact that the number of centres increases with exposure necessitates the assumption that they have differing sensitivity to light. Silberstein [61] attempted to apply an extreme concept of light quanta to the photographic process. According to him a centre is formed and a grain becomes developable every time a light energy quantum—a "light dart"—hits the surface of the grain. His theory now seems to be entirely disproved. Experiments of Trivelli and Righter,[62] who measured the yield of such collisions in one-grain-layer plates, showed that not more than 0.0001 of the exposed area of the grains is sensitive to light.[63] Toy [64] showed, furthermore, that the sensitivity of an emulsion to decreasing wave lengths does not decrease, which it should according to the "dart" theory, but increases towards the ultraviolet, being approximately proportional to the amount of light energy *absorbed* by the emulsion. The degree of accuracy in Toy's experiments did not permit a decision between the proportionality to the energy or to the number of quanta absorbed. Besides, since his measurements were carried out with plates developed after illumination, a determination of the quantum yield was impossible.

In recent years, an application of the more general quantum theory to photographic emulsions has been repeatedly attempted. In contradistinction to the problems already discussed, measurement of the quantum yield excluded the use of developers for the intensification of the light action. Silver formed during the photochemical reaction had to be measured directly. The method generally used in the experiments about to be considered included treating the illuminated emulsion with a fixing solution, thus laying bare the silver formed both at the surface and in the interior of the grains, dissolving the silver in nitric acid, and subsequently titrating the silver.

Notwithstanding the similarity of their experimental methods, different investigators arrived at widely varying conclusions. Weigert and his co-workers suggest that a quantum yield approximately equal to unity is obtained only under very special conditions, the efficiency otherwise being much lower. Eggert and Noddack maintain that the yield decreases below the theoretical value of 1.0 only on very inten-

[60] *Phil. Mag.*, 44, 352 (1922).
[61] *Ibid.*, 44, 257 (1922); see also Lowry, *Phot. J.*, 62, 193 (1922).
[62] See Sheppard, Trivelli and Wightman, *Trans. Farad. Soc.*, 19, 296 (1923).
[63] These measurements of course are not of the "quantum yield" since only the incident light intensity and not the absorption was measured.
[64] *Trans. Farad. Soc.*, 19, 290 (1923).

sive illumination. This difference of opinion is due to the difficulties in estimating the actual light absorption by the silver halides in a finely dispersed system, where the light scattering is increased to a very appreciable proportion. A rough estimate of the light actually absorbed in the technical silver bromide plates led Eggert and Noddack [65] to a value of about 5-10 per cent for the wave length 4080 Å., which, when compared with the amount of silver formed, indicated a quantum yield of approximately unity. Weigert,[66] however, demonstrated that absorption amounted to about 80 per cent for this wave length, thus leading to a quantum yield much lower than unity. A reinvestigation of the problem by Eggert and Noddack [67] confirmed Weigert's value, the authors suggesting, however, that the absorption is due largely to the gelatin and that only light energy absorbed by silver halides is photochemically active. The actual measurements revealed that: (a) molten silver bromide absorbs only light of shorter wave length than 4660 Å.; silver chloride absorbs light below 4050 Å.; (b) pure silver bromide photographic plates are sensitive to light only below 4660 Å.; silver chloride plates, below 4050 Å.; (c) pure gelatin in thickness of 1.57 mm. shows the following absorption: [68]

TABLE 6.

Wave length	6150	5460	4900	4360	4050	3650	Å.
Absorption	24	32	42	62	88	94	per cent

(d) photographic plates show a marked absorption of light increasing from 6150 Å. towards the shorter wave lengths. Eggert and Noddack suggested therefore that the light absorption by emulsions was largely and at longer waves even exclusively, due to gelatin, the actual path of light in the thin photographic layer being much longer than the measured thickness, on account of manyfold reflections of the light by the silver halide particles.

Using the absorption values for pure gelatin and assuming Lambert's law valid for the plates, the separate absorption by gelatin and, from this, the absorption by the halides in different spectral regions can be calculated, if the assumption be made that at 6150 Å., the light absorption is due entirely to gelatin. In the following table, some of Eggert and Noddack's results are given, the values in parentheses referring to a silver chloride emulsion which had approximately the same size of particles and the same weight of halide and gelatin per unit of surface as the bromide plate used.

[65] *Sitzb. Preuss. Akad.*, 631 (1921).
[66] *Z. physik. Chem.*, 99, 499 (1922).
[67] *Z. Physik*, 20, 299 (1923); 21, 264 (1924); 31, 922 (1925).
[68] The absorption varies considerably with the kind of gelatin employed.

TABLE 7. *"Agfa Reproduction" Silver Bromide Emulsion and a Special Silver Chloride Emulsion.*

Wave length	Scattered %	Transmitted %	Absorbed %		
			Total	Gelatin	Halide
6150 Å.	59 (60)	29 (28)	12 (12)	12 (12)	0 (0)
5460	61 (62)	24 (24)	15 (14)	17 (17)	−2 (−3)
4900	60 (62)	20 (20)	20 (18)	23 (23)	−3 (−5)
4360	41 (57)	11 (9)	48 (34)	37 (37)	+11 (−3)
4050	23 (45)	8 (4)	69 (51)	53 (53)	+16 (−2)
3650	12 (15)	4 (1)	84 (84)	74 (74)	+10 (+10)

Weigert [69] criticised the method of obtaining these values. He suggested that the absorption coefficients and not the absorption should be used in calculating the partial absorptions of gelatin and silver halides (comp. page 39 on quinine and chromic acid) and that Eggert and Noddack's method yields values for the halides which are too low. The applicability of Lambert's law is also doubtful, inasmuch as an equal scattering power of halide particles for all wave lengths must be assumed. Since the scattering power usually increases with decreasing wave length, this correction would tend to decrease the values of Eggert and Noddack and possibly both corrections would more or less balance each other. The titration of the silver formed photochemically and a calculation of the number of absorbed quanta, led Eggert and Noddack to a value of quantum yield equal to unity for the wave lengths 4360, 4050 and 3660 Å. in the case of silver bromide, and for 3660 Å. in the case of chloride. A slow decomposition of chloride in the light of wave lengths 4360 and 4050 Å. was also noticed and, from its rate, it was concluded that if the equivalence law is valid in this case about 0.3 per cent of the light 4360Å. and about 1.0 per cent of 4050Å. are absorbed by the silver chloride.

The yield in the case of bromide was found to be unchanged within the limits 3.9×10^{15} to 30×10^{15} absorbed quanta per square cm., with longer exposures the quantum yield decreasing, however, to 0.06 for 5×10^{19} quanta per sq. cm.[70] After a treatment of bromide plates with water, alkali, etc., the quantum yield could be maintained equal to unity for higher numbers of absorbed quanta. The decrease in the yield for the chloride emulsions was less marked, the same value being obtained between 1.1×10^{15} and 147×10^{15} quanta absorbed per sq. cm.

[69] *Z. Physik*, 18, 232 (1923).
[70] Essentially identical results have been obtained by Eggert and Noddack using a different kind of silver bromide emulsion. *Loc. cit.*

A very slow decomposition of silver iodide emulsions indicated a very low yield even for the initial stages of illumination.

Weigert and his co-workers,[71] studying the action of light on emulsions used in daylight photographic papers and consisting of very finely dispersed silver chloride (1.0 part) and soluble salts of silver (2.6 parts) with nitric, citric and tartaric acids distributed in the gelatin, arrived at quite different conclusions as to the nature of the light action. The amounts of silver formed plotted against time of illumination yielded an S-shaped curve, thus indicating an autocatalytic process. The amount of silver chloride remained unchanged, apparently only the soluble salts being decomposed. These observations, together with the fact that the total absorbed number of quanta was higher than the number of silver atoms formed, led Weigert to the theory, that silver chloride is not light sensitive and that only light absorbed by the metallic silver present acts photochemically.[72] Calculation of the energy absorbed by silver indicated that at very small quantities of the latter the yield was of the order of unity.

Contradictory results were obtained by Eggert and Noddack,[73] who repeated Weigert's experiments. No S-shaped curve could be observed and the authors suggested that systematic errors in silver determinations caused this effect in Weigert's experiments. The light absorption of silver chloride calculated as before was found to be very small, amounting to 5 per cent for the light 3660 Å. Accordingly, the yield calculated from the number of silver atoms formed divided by the total number of incident quanta was of the order 1×10^{-2} for the light 4360 Å.; 2×10^{-2} for 4050 Å.; and 6×10^{-2} for 3660 Å. No variation in the yield could be observed when the number of incident quanta was varied from 1×10^{15} to 180.10^{15} per sq. cm. As to the constancy of the silver chloride mass in Weigert's experiments, the authors suggested that all chlorine atoms formed by the action of light recombined with silver from the soluble salts to give silver chloride.

As seen from the foregoing, Eggert and Noddack interpreted their results by introducing the concept of light energy quanta into the otherwise essentially unchanged theory of Carey Lea and Lüppo-Cramer. According to Eggert and Noddack, absorption of one quantum of light energy by a halide particle always results in the decomposition of one silver halide molecule. The halide atoms are subsequently absorbed by gelatin or some other "acceptor" present in the emulsion. Since,

[71] *Sitzb. Preuss. Akad.*, 641 (1921); Schubert, Dissertation, Leipzig (1923).
[72] For similar views comp. W. Ostwald, *Lehrb. allgem. Chem.*, II, 267 (1911); Renwick, *J. Soc. Chem. Ind.*, 39, 156T (1921).
[73] *Z. Physik*, 31, 922; 942 (1925).

with increasing time of illumination, the acceptors become more and more saturated, the halide atoms occasionally recombine with silver atoms and finally a decrease in the quantum yield must be observed. This is more or less prevented by addition of water, alkali, etc., all of which act as acceptors. The action of acceptors is most energetic when chlorine atoms are formed; and, therefore, particularly in the presence of large amounts of acceptors (as soluble silver salts in daylight photographic papers) visible images can easily be obtained by use of a silver chloride emulsion. Bromine and, even more so, iodine atoms react less readily with acceptors; instead, they recombine with silver atoms, and therefore no visible image can be obtained by the use of silver bromide or iodide emulsions. The fate of the silver atoms produced is that they are adsorbed by the adjacent ions in the crystal lattice. This new complex, somewhat similar to the hypothetical subhalides, but, of course, having no definite molecular weight, has new properties; as, for instance, an absorption band shifted to longer wave lengths in comparison with that of "pure" silver halide, thus accounting for the observed shift of sensitivity to longer waves. In the experiments of Fajans, which we shall discuss subsequently, we shall find definite confirmation of this concept of the products of light action on silver halides.

Certain difficulties present themselves, however, when the attempt is made to combine Eggert and Noddack's observations with those on developed emulsions. The former authors find that the quantum yield is the same for two widely different silver bromide emulsions. Microscopic studies, on the other hand, reveal that the sensitivity of grains is widely varying. Of course an increase of sensitivity with the size of the grains may be explained by an increased light absorption in larger grains, but such explanation is inadequate when considering grains of essentially the same size and shape and, it should be remembered, of the same crystalline structure. Furthermore, the observed distribution of the development centres on the surface of the grains deviates somewhat from that distribution of silver atoms which should be expected if the absorption of light quanta by silver halide molecules occurred according to the laws of chance and was proportional to the local density of radiation. Finally, Svedberg, and Slade and Higson obtained S-shaped curves by plotting the number of developed grains against exposure. These results likewise do not agree with the linear relation observed by Eggert and Noddack. Instead they support the previously mentioned experiments of Weigert.

Do these discrepancies indicate a necessity of revision of Eggert

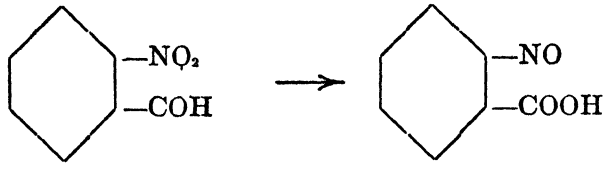
and Noddack's experiments or do they show that not all silver atoms formed on the surface of the grains[74] become development centres, and that some other factors besides the presence of silver atoms play a determining rôle in the development process?

The photochemistry of the solid state is not limited to the action of light on photographic emulsions; but only a very few reactions of this type have received as much detailed attention from the point of view of the equivalence law.

The Action of Light on Cinnamylidene Malonic Acid. Bowen and co-workers[75] studied the change of cinnamylidene malonic acid in crystalline form under the action of violet and blue light 4000-4500 Å.

This substance has a dark yellow color and strongly absorbs light of the wave lengths employed. On illumination, it becomes colorless, probably polymerising. Bowen and his co-workers estimated the quantum yield to be about 0.79, but pointed out that this figure is somewhat low, since the substance, in the form of a thin layer of compressed fine crystals, shows a marked scattering of light. The scattered light was included by Bowen in his calculation of absorbed light.

The Isomerisation of *o*-nitrobenzaldehyde. The same authors studied also the isomerisation of *o*-nitrobenzaldehyde to *o*-nitrosobenzoic acid:



in crystalline form. The calculation of the quantum yield led to a figure of 0.5, the second and a more accurate series yielding the value 0.69. The authors point out that in the case of *o*-nitrobenzaldehyde the scattering of the light (4000-4500 Å.) is larger than in the case of cinnamylidene malonic acid, since the colour of the former is a much lighter yellow. They suggest that actually the quantum yield is close to unity. Padoa[76] noticed that the time of decomposition of single crystals of o-nitrobenzaldehyde under the action of linearly polarised light is dependent on the position of crystal axes relative to the plane of polarisation. Bowen and co-workers interpret this observation by suggesting that the absorption coefficients of light are different for different planes of polarisation of light, a phenomenon well known

[74] Comp., however, Eggert and Noddack, *loc. cit.*
[75] *J. Chem. Soc.*, 125, 1218 (1924).
[76] *Atti accad. Lincei.*, 28, 872 (1919).

in turmaline crystals. They consider as untenable the other possible explanation, namely, that only light of a definite plane of polarisation is effective in causing the chemical change, since, in a mass of crystals distributed at random, the quantum yield should then be equal to 0.5; their measurements indicate a higher value. Weigert and Brodmann [77] arrived at a different conclusion measuring the quantum yield of the isomerisation of *o*-nitrobenzaldehyde in acetone solutions. The yield was found to be independent of the concentration [78] and of the wave length. The yield obtained was close to 0.5 for the mercury lines 3660, 4050 and 4360 Å.

To account for this yield, Weigert and Brodmann assume that only those randomly distributed benzaldehyde molecules absorb radiation in which the plane of NO_2—COH groups is perpendicular to the light beam and that, further, only those molecules undergo the isomerisation in which the direction NO_2—COH, at the moment of light absorption coincides with the direction of the electric vector of the electro-magnetic light waves. If this mechanism be accepted, the quantum yield must be, of course, 0.5.

Trying to interpret the observed quantum yield by means of a more general assumption, not involving the geometrical considerations to Weigert, it could be suggested that the probabilities for an excited benzaldehyde molecule to undergo the isomerisation or to return to the original state are equal to one another. This suggestion is, however, a mere statement and does not bring us nearer to the understanding of the actual reaction mechanism. On the basis of Weigert's theory, however, it should be expected that the quantum yield is completely independent of the wave length of incident light and other conditions of the experiments.

The concept of primary formation of activated molecules on the other hand admits a possible influence of different physical factors on the quantum yield of the reaction. If one value of Weigert's measurements in the light 4360 Å. be excluded as rather definitely out of line (0.65), we then find the following mean values of the quantum yield for different wave lengths.

TABLE 8.

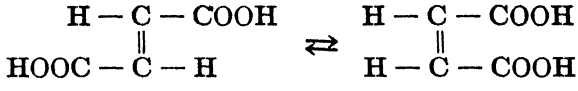
Wave length	3660	4060	4360 Å.
Quantum yield	0.539	0.474	0.455 (0.477)
Number of experiments	14	7	9 (10)
Average deviation	±0.047	±0.043	±0.038 (±0.055)

[77] *Trans. Farad. Soc.*, 21, 453 (1925).
[78] Comp. Weigert and Kummerer, *Ber.*, 46, 1207 (1913).

The apparent decrease of the quantum yield with increasing wave length lies thus almost within the experimental errors. A possible effect of other variables on the reaction velocity was investigated only by Berger,[79] who observed that addition of neutral salts to aqueous-acetone solutions of *o*-nitrobenzaldehyde affected a decrease of the rate of reaction, but the decrease never exceeded 10 per cent and was close to the limit of experimental error.

It has frequently been suggested that reactions involving only some intramolecular displacement and being thus "unimolecular" should, more readily than other types of photochemical reactions, follow the equivalence law. The results of the studies on *o*-nitrobenzaldehyde indicate, however, more complicated kinetic relations.

Maleic-Fumaric Acid Transformation. An even more striking deviation from the equivalence law was observed by Warburg[80] in the isomeric changes of maleic and fumaric acids:



Here a quantum yield of only 4 to 13 per cent of the calculated was obtained. The results of Warburg are represented in the following tables.

TABLE 9. *Fumaric into Maleic Acid.*

Wave length Å.	Concentration (F. acid)	Quantum yield $\frac{\text{molec.}}{\text{quantum}}$
2070	0.01020	0.104
	0.00306	0.080
2530	0.01020	0.098
	0.00306	0.087
2820	0.01020	0.134
	0.00306	0.099

TABLE 10. *Maleic into Fumaric Acid.*

Wave length Å.	Concentration (M. acid)	Quantum yield
2070	0.01020	0.032
	0.00514	0.037
2530	0.01020	0.043
	0.00514	0.048
2820	0.01020	0.032
	0.00514	0.035

On the whole, the influence of concentration and wave length is opposite for both reactions, the quantum yield slightly increasing with wave length and concentration in Table 9 and decreasing in Table 10.

[79] *Rec. trav. chim.*, 44, 49 (1925).
[80] *Sitzb. Preuss. Akad.*, 860 (1919).

As a general explanation of his results, Warburg suggested that the molecules of both acids were decomposed into H—C—COOH groups on absorption of radiation according to the requirements of the equivalence law, but that the observed rate of isomeric change was determined by the relative probabilities of the free groups on collision to return to the original molecule or to form the isomer. The theory provides in a general form for the influence of concentration and of wave length and (a possible) influence of the solvent. The data in the tables agree well with a deduction from Warburg's theory that a change in physical condition of the reacting system (concentration, wave length) resulting in an increase of the quantum yield of the reaction A should decrease the yield of the reaction B.

However, unless an incomplete loosening of the bond C = C is assumed, the theory does not account for the low quantum yield of *both* reactions under the same physical conditions, since, according to it, the quantum yields in this case should be related by the equation

$$\varphi_1 + \varphi_2 = 1.$$

It is possibly significant that the endothermic transformation fumaric → maleic acid has, throughout, a higher quantum yield than the opposed reaction.

Allotropic Transformation of Sulfur. Another photochemical reaction of a similar chemical type: the allotropic transformation of the soluble sulfur $S\lambda$ into insoluble $S\mu$, studied by Wigand,[81] is complicated by the measurable speed of the reverse thermal reaction $S\mu \rightarrow S\lambda$. Besides, the colloidal particles of $S\mu$, suspended in the solution, scatter light and, therefore, the light energy actually absorbed by $S\lambda$ is decreased to an uncontrollable extent during the reaction. Only by extrapolation to the initial moments of illumination is a quantitative study of the kinetics made possible. The violet and near ultraviolet spectral region, which is effective in this reaction, is not uniformly absorbed by sulfur solutions. The mercury line group around 4060 Å. is only slightly and the ultraviolet completely absorbed. Accordingly, in light of a mercury lamp, the order of reaction in the initial stage was found by Wigand to be less than unity.

The quantum yield was not measured by Wigand, but later calculations of Warburg [82] indicate a value of a similar magnitude as in the maleic acid isomerisation: 0.07.

The solvent exerts apparently a marked influence on the rate of reaction, since the values obtained in carbon disulfide, carbon tetra-

[81] *Z. physik. Chem.*, 64, 455 (1909); 77, 428 (1911).
[82] *Sitzb. Preuss. Akad.*, 960 (1919).

chloride and benzene varied in the ratio of 1:1.14:1.31. The treatment of the reaction kinetics is further complicated by the unknown composition of the insoluble sulfur Sμ. Wigand suggested for this the same molecular weight (S_8) as is known to be the weight of the soluble modification (Sλ), but the evidence is not convincing.

Decomposition of Acetaldehyde. Recently Bowen and Watts [83] claimed that a quantum yield close to unity is characteristic for two gaseous reactions, the decompositions of acetaldehyde and of acetone.

The decomposition of acetaldehyde was studied already by Berthelot and Gaudechon,[84] more extensively, however, in the liquid phase. The relations observed were rather complicated. In the light of longer wave length than 3000 Å., acetaldehyde is, for the largest part, decomposed into CO and CH_4, only traces of C_2H_6, etc., being found among the reaction products. Shorter wave lengths (3000-2500 Å.) cause a polymerisation and a partial oxidation of acetaldehyde, even in absence of oxygen, to acetic acid. Apparently, we are dealing here with a case of inner oxidation, the oxygen atom being displaced from one molecule of acetaldehyde to another. The short waves, <2500 Å., cause a rapid polymerisation to paraldehyde and metaldehyde. In presence of water, the polymerisation is suppressed, but the oxidation is increased and, besides, some water soluble dark coloured substances are formed. Since Berthelot and Gaudechon used mercury in their reaction vessels the possibility is not excluded that these reactions are due, at least partly, to the photosensitising action of mercury vapor (Chapter IV).

Bowen and Watts observed, in the vapour of acetaldehyde, two reactions proceeding under the action of unfiltered ultraviolet light of a mercury lamp. One is the decomposition to CO and CH_4, the other a polymerisation, and the authors assume that this goes by:

$$CH_3COH + h\nu \rightarrow (CH_3COH)'$$
$$(CH_3COH)' + 2CH_3COH \rightarrow \text{polymerisation product.}$$

The decrease in pressure of unsaturated acetaldehyde vapour indicates the difference of the rates of both simultaneous reactions, whereas the increase of pressure of saturated vapor in presence of liquid acetaldehyde is the measure of the decomposition reaction only. Assuming the scheme of Bowen and Watts to be correct, we have

$$(1)\quad -\frac{dp}{dt} = 3y - x$$
$$(2)\quad +\frac{dp}{dt} = x$$

[83] *J. Chem. Soc.*, 127, 1607 (1925).
[84] *Compt. rend.*, 156, 68, 233 (1913).

In these equations y is the fraction which undergoes polymerisation and x the decomposing fraction of activated molecules. The total rate of reaction of activated molecules being $y + x$, Bowen and Watts find that this sum in their experiments is equal to 1.87×10^{15} molecules per sec. The estimate of the number of absorbed quanta was attained by means of an actinometer, i.e., by measuring the difference of the rates of reaction in a photochemical system of a known quantum sensitivity placed behind the main reaction vessel, this latter being alternatively emptied and filled with the reacting gas.

As actinometer, the oxidation of oxalic acid in presence of uranyl salts was chosen. We may note that this method of study is not very exact. Besides the error caused by an erroneous determination of the quantum yield of the actinometer system, a similarly important error can be involved in the calculations, if the absorption spectrum of the photosensitive component of the actinometer liquid is different from that of the reaction system studied. Only if all wave lengths causing a decomposition of the gas are strongly absorbed by the actinometer, will this method yield consistent results. It is of course obvious that the absorption of light by the reacting mixture will be found too small if a frequency absorbed by it is ineffective in the actinometer.

Using the actinometer, Bowen and Watts calculated the number of quanta absorbed by acetaldehyde to be 0.87×10^{15}, the quantum yield for the mean wave length 3130 Å. being thus 2.17. It seems to be difficult to reconcile the proposed reaction mechanism with this measured quantum yield two. A further investigation of the quantum efficiency together with a more quantitative study of the reaction products is desirable.

The decomposition of gaseous acetone in ultraviolet light studied by Bowen and Watts by means of the same actinometer showed varying quantum yields depending on the pressure. At higher pressures the yield was found to be about 1.7, and at lower pressures, at room temperature, about 0.41. The products of reaction have not been quantitatively studied.

Decomposition of the Permanganate Ion. In an interesting research, Rideal and Norrish [85] tried to demonstrate the validity of the equivalence law in the photochemical decomposition of permanganate ion under the action of ultraviolet light. Rideal and Norrish claim that the visible spectrum, in which permanganate ion shows several absorption bands, is photochemically ineffective, but that ultraviolet light around 3130 Å., where permanganate possesses another absorp-

[85] *Proc. Roy. Soc.*, 103A, 342, 366 (1923

tion maximum, leads to its decomposition and a formation of a colloid, which, after drying, has the composition $K_2O.2MnO_2$.

Although the effective radiation is completely absorbed in the 1/100 *N* solution of neutral potassium permanganate studied, the rate of reaction is unimolecular with respect to permanganate ion, being thus apparently not proportional to the absorbed light energy.

Rideal and Norrish suggested, however, that, in reality, the rate of reaction is proportional to the amount of absorbed light energy, but that when reaction proceeds, the scattering of light by the colloidal particles of MnO_2 formed increases very rapidly and thus the light energy actually absorbed by permanganate decreases.

They assume that the rate of reaction is given by the following equation:

$$(1) \quad -\frac{d[MnO_4^-]}{dt} = k_1 (I_{\text{incident}} - I_{\text{scattered}})$$

and further that:

$$(2) \quad I_{\text{scattered}} = k_2 ([MnO_4^-]_0 - [MnO_4^-]_t)$$

This last equation is approximately true only when the number of colloidal particles is proportional to the amount of permanganate decomposed and their size therefore remains constant throughout the course of reaction.

It is easy to deduce from equations (1) and (2) the equation for the rate of reaction:

$$(3) \quad -\frac{d[MnO_4^-]}{dt} = k_1 k_2 [MnO_4^-]_t + k_1 (I_{\text{incid.}} - k_2 [MnO_4^-]_0)$$

It is obvious that this equation will represent the experimental results of Rideal and Norrish only if the second term on the right side is equal to zero; the scattering power has thus a definite value. Besides, the authors themselves demonstrated that the assumption that the size of the colloidal particles remains constant during the reaction is true only for a short initial period of illumination. Finally, we find in the paragraph dealing with the measurements of the absolute amount of absorbed energy, a statement (p. 374, *loc.cit.*) that the amount of energy transmitted by the solution increases with time of illumination. This experimental result directly opposes the view of the authors that the scattering power of formed colloidal particles is so large that it can account for the unimolecular course of the reaction.

Summarising we see that the arguments advanced in favour of the proportionality of the reaction rate and light energy absorbed are rather doubtful. The authors nevertheless measured the quantum

yield, finding for the combined effect of the mercury lines 3650, 3128 and 2536 Å., a mean value of about 0.2.

In presence of oxalic acid, Rideal and Norrish observed a much more rapid reaction, but the kinetics of this process were not quantitatively studied.

More promising for an application of the equivalence law seems to be the decomposition of permanganate in acid solutions. This reaction is not complicated by a formation of colloidal manganese dioxide, which is rapidly coagulated by the acid. The data of Rideal and Norrish indicate that, as long as acid is present in the solution, the rate of reaction is independent of acid concentration. The same result was obtained with respect to permanganate concentration, which is shown in the following table.

TABLE 11. $KMnO_4$:0.01*N*. H_2SO_4 1.0*N*.

Time	0	20	40	60	80	100	120
[$KMnO_4$]	0.01000	0.00860	0.00708	0.00535	0.00394	0.00254	0.00145
$\frac{\Delta c}{\Delta t}$		0.0070	0.0076	0.0086	0.0070	0.0070	0.0060

A slight decrease of the rate of reaction at the end is probably due to incomplete light absorption.

The data contained in the paper of Rideal and Norrish allow an approximate calculation of the quantum yield of the acid reaction. For the above-mentioned wave lengths the resulting value is not far from 0.5. The mechanism of the neutral reaction was interpreted by the authors as follows:

(1) $MnO_4^- + \text{light energy} \rightarrow MnO_2 + 2O + \text{electron}$
(2) $\frac{1}{2}\ H_2O + O + \text{electron} \rightarrow 2OH'$
(3) $O + O \rightarrow O_2$
(4) $MnO_2 + H_2O \rightarrow MnO_3H_2$
(5) $MnO_3H_2 + KOH \rightarrow MnO_3KH + H_2O$
(6) $2MnO_3KH \rightarrow Mn_2O_5K_2 + H_2O$

From the point of view of energy an objection can be advanced against reaction (1), since the energy of effective wave lengths (about 90,000 cal.) is undoubtedly insufficient for the formation of two oxygen atoms and an electron, unless an accumulation of absorbed energy by activated MnO_4^- ions takes place.

THE EQUIVALENCE LAW AND THE STATIONARY STATE

The study of all reactions which we have discussed so far, with the exception of the sulfur modifications and the neutral decomposition of permanganate, was simplified by the circumstance that, in the experimental conditions actually used, the observed rate of reaction,

minus a small correction for the simultaneously occurring thermal process, was a direct measure of the rate of photochemical reaction. The photochemical literature contains, however, many descriptions of photochemical reactions, where the illumination, after an initial change in the concentrations of the reactants, leads to the formation of an equilibrium, which, being once reached, remains unchanged by further illumination.

The concept of a "photochemical equilibrium" undoubtedly played an important rôle in the theoretical development of photochemistry. In earlier theories of the chemical actions of light much attention was paid to these equilibria, since it was generally expected that they would be the most convenient material for the application of classical thermodynamics to photochemistry.

Nernst [86] for instance defined photochemical equilibria similarly to thermal ones and gave, as a general expression for the rate of a photochemical reaction, the equation:

$$V = kc_1^{n_1} c_2^{n_2} \ldots \text{——} k^1 c_1^{1 n_1^1} c_2^{1 n_2^1} \ldots,$$

in which k and k^1 were supposed to be certain functions of the light intensity.

Theories of photochemical equilibria more closely related with the modern concept of the phenomenon were developed by Luther and by others, but we shall not enter into detailed discussion of them.

In his thermodynamic derivation of the equivalence law, Einstein also assumed that the chemical system under consideration was in a state of equilibrium and that, as a result of increased density of a particular radiation frequency, a new, thermodynamically definable, equilibrium was reached in a reversible way. From the point of view of the quantum theory, photochemical equilibria must therefore be possible. They must be, however, limited to the particular type of reactions defined by Einstein: a completely reversible system in which the thermal process is followed by emission of the same frequencies of radiation which are causing the original photochemical reaction. In actual fact, no reactions of this type have been observed so far (excepting the phenomena of resonance radiation as not strictly photochemical processes). It was found, instead, that, even in endothermic photochemical reactions, only a small fraction of the radiation energy is utilised for chemical work and that by far the larger fraction is irreversibly transformed into heat energy of lower temperature.

Thus, in photochemical "equilibria" studied, the free energy of

[86] "Theoretical Chemistry," 4th edition.

the whole system (including radiation energy) is continually decreasing instead of being independent of time, as in real thermal equilibria.

Accordingly, we encounter only few of the properties of the thermal equilibria in photochemical equilibria: the equations of the mass action law, although found to hold for some particular cases, are, in general, in disagreement with the experimental observations; material catalysts, even those which are not absorbing light themselves, can change the position of a photochemical equilibrium; finally, the equilibrium concentrations of the reactants are, in general, dependent on the shape and size of the reaction vessel.

Already these properties are sufficient support for the suggestion that the expression "photochemical equilibrium," often used in the literature, does not represent the actual relations, and that, instead, the expression "stationary state" is more in agreement with the experiments. Two essential types of photochemical stationary states can be conveniently distinguished, although they do not differ in principle. In one type, the photochemical reaction is opposed by a spontaneous thermal process and the stationary state is a result of two factors distinctly different in nature. From theoretical considerations we must conclude that the stationary concentrations of the reactants will be different from the corresponding values of the thermal equilibrium and that the position of the stationary state must be dependent on the intensity of illumination (all other factors remaining constant).

Further, every factor increasing the rate of thermal reaction will bring the photochemical stationary state closer to the thermal equilibrium. The temperature will have, for instance, such an effect, since the temperature coefficients of dark reactions are, as a rule, larger than those of photochemical reactions. It is obvious that for every photochemical stationary state a temperature must exist where no shift from thermal equilibrium can be realised by illumination and that this is the temperature of the reacting body which is equal to the "black body" temperature of incident radiation. The study of this type of photochemical stationary states is greatly simplified by the fact that the thermal process can be usually studied apart, and then, from the combined effects of dark and light reactions, the kinetics of the latter derived. In this kind of experimental investigation, the implicit assumption is frequently made that the rates of thermal and photochemical reactions are simply additive. Plotnikoff [87] for instance considers the rule of additivity of thermal and photochemical reactions as one of the fundamental laws of photochemistry.

[87] *Z. physik. Chem.*, 58, 214 (1907); 64, 215 (1908).

In one of the subsequent chapters, we shall see that this is not always so and that reactions exist in which the thermal and photochemical rates are not superposed but combine according to more complicated schemes. In the meantime, we shall assume that the results obtained by subtraction of the thermal rate from the integral velocity observed on illumination represent actually the pure photochemical reaction rate. This is in general admissible, since the above-mentioned deviations are due to a particular reaction mechanism, and are not generally applicable.

The other type of photochemical stationary states will include those processes in which both opposed reactions acquire a measurable speed under experimental conditions only by action of radiation from an outside source. Results of experimental studies indicate that in most of these reactions the spectral regions effective for opposed processes are different and this facilitates the separate study of single reactions. In other cases, however, the absorption spectra of the different reactants overlap each other to such an extent, that no separate study of the single processes can be realised unless only the components of one reaction are present in measurable quantities. Not much quantitative work has been done on the great variety of photochemical processes leading to a stationary state and only in a few cases has the quantum yield been determined.

The Decomposition of Nitrosyl Chloride. Among these, the only reaction in the gaseous phase is the decomposition of nitrosyl chloride. Trautz [88] and his co-workers have extensively studied the dark kinetics of the system:

$$2NO + Cl_2 \rightleftarrows 2NOCl.$$

They came to the conclusion that the formation of nitrosyl chloride occurred in an apparently trimolecular reaction, but suggested that the actual mechanism consists in a sequence of bimolecular processes. The rate of this reaction is readily measurable even at room temperature and since the equilibrium constant

$$K = \frac{[NO]^2\,[Cl_2]}{[NOCl]^2}$$

is small at lower temperatures, an almost complete formation of nitrosyl chloride takes place.

Kiss [89] observed that nitrosyl chloride could be partially decomposed by illumination with visible light. The decomposition was

[88] *Z. anorg. Chem.*, 88, 285 (1914); 97, 241 (1916); 110. 248 (1920).
[89] *Rec. trav. chim. Pays Bas*, 42, 665 (1923).

not complete and, on longer illumination, a stationary state was reached. The degree of light absorption was not studied by Kiss who suggested, however, that the rate of decomposition on illumination was well represented by the equation:

$$-\frac{d\,[\mathrm{NOCl}]}{dt} = k_1\,[\mathrm{NOCl}] - k_2\,[\mathrm{Cl_2}]\,[\mathrm{NO}]^2$$

Of the two constants, k_2 is the known constant of the thermal rate of formation of nitrosyl chloride. The unimolecular character of the pure light reaction would suggest that the unfiltered radiation of an incandescent lamp in the experiments of Kiss was only slightly absorbed by nitrosyl chloride. By means of this equation, Kiss determined also the temperature coefficient of the photochemical reaction and found it equal to 1.0 over the temperature range of 0-78° C

Later, Bowen and Sharp [90] reinvestigated the photochemical reaction using filtered light of the spectral region 4380-5000 Å., which they found to be very strongly absorbed by nitrosyl chloride. Instead of using mixtures of this latter with chlorine, as did Kiss, Bowen and Sharp studied the decomposition of pure nitrosyl chloride and observed a zero order reaction up to 10 per cent decomposition. The comparison of the rate of reaction with the absolute amount of light energy absorbed revealed that about two molecules of nitrosyl chloride are decomposed per absorbed quantum.

The absorption spectrum of nitrosyl chloride contains, in addition to a strong continuous absorption below about 5300 Å., several weak bands in the region 5300-6200 Å. Bowen and Sharp failed to observe any reaction under the influence of these last wave lengths, but ascribed the negative result to the small amount of light energy which was absorbed by nitrosyl chloride in the experiment. Bowen and Sharp argued on the basis of their own experiments that in the experiments of Kiss also the light absorption by nitrosyl chloride was practically complete and that his results should be represented not by a unimolecular but by a reaction of zero order.

Indeed, applying the equation:

$$-\frac{d\,[\mathrm{NOCl}]}{dt} = k_1 - k_2\,[\mathrm{NO}]^2\,[\mathrm{Cl_2}]$$

to the experimental data contained in the publication of Kiss, we find a reasonably good constancy of k_1. As an example, the contents of Kiss' Table 1 may be represented in a summarised form:

[90] *J. Chem. Soc.*, 127, 1026 (1925).

TABLE 12.

Initial pressures: NOCl 418.9 mm.; Cl_2 36.8 mm.

Time min.	$\Delta p \frac{mm.}{min.}$	k_1	Time min.	$\Delta p \frac{mm.}{min.}$	k_1
2.0	0.75	0.75	62.0	0.18	0.27
12.0	0.31	0.31	72.0	0.17	0.29
22.0	0.96	0.27	101.0	0.13	0.30
32.0	0.98	0.30	120.5	0.051	0.20
42.0	0.22	0.26	136.0	0.058	0.33
52.0	0.93	0.30	154.5	0.032	0.31

The initial high value is probably due to the thermal expansion of the gases on illumination. Bowen and Sharp consider as a probable reaction mechanism the following sequence of reactions:

$$NOCl + h\nu \rightarrow NO + Cl$$
$$NOCl + Cl \rightarrow NOCl_2$$
$$NOCl_2 \rightarrow NO + Cl_2$$

of which the first requires 45,000 cal., or less than is supplied in the form of quantum energy.*

The Equilibrium. $Fe^{\cdot\cdot} - Fe^{\cdot\cdot\cdot}$, $I_2 - I^-$. Another case of a dark-light stationary state, which has been well studied, is the action of iodine on ferrous salts. The dark reaction is reversible and an equilibrium is slowly reached in aqueous solutions according to the equation:

$$2Fe^{\cdot\cdot} + I_2 \rightleftarrows 2Fe^{\cdot\cdot\cdot} + 2I^-.$$

Sasaki [91] noticed that the oxidation of iodine ion is retarded by visible light and that the reduction of iodine is accelerated, a different equilibrium constant being obtained on illumination.

Rideal and Williams [92] studied, in a more quantitative way, the photochemical reaction, using monochromatic light of wave length 5790 Å. On illumination of the dark equilibrium mixture (obtained by dissolving a ferric salt and potassium iodide in dilute sulfuric acid and allowing time for the completion of the dark reaction) the concentration of iodine decreases until a stationary state is reached, indicating a reduction of iodine by ferrous ions. Theoretically, the rate of reaction in light can be represented as the result of four separate reactions:

* Dr. G. Carlo and the writer have studied recently (unpublished) the absorption spectrum of nitrosyl chloride. No continuous absorption could be discovered, contrary to the affirmation of Bowen, in the region investigated: 7000-3500 Å. The absorption spectrum consists here of numerous well defined bands. This must be interpreted as indicating that excited molecules are formed on light absorption and that no immediate dissociation, in the sense suggested by Franck (see the first chapter), does take place.

[91] *Z. anorg. Chem.*, 122, 61 (1922).
[92] *J. Chem. Soc.*, 127, 258 (1926).

$$([I_2 + 2Fe^{\cdot\cdot} \text{ (light)}] + [I_2 + 2Fe^{\cdot\cdot} \text{ (dark)}]) - ([I^- + Fe^{\cdots} \text{ (dark)}] + [I^- + Fe^{\cdots} \text{ (light)}])$$

Of these, the two dark reactions have already been objects of kinetic study.[93] Their mechanism is not simple, according to Wagner,[94] who extended the earlier measurements. He found that the rate of dark oxidation of the iodide ion is represented by the following equation:

$$(1) \quad -\frac{d[I^-]}{dt} = 2k_1 \frac{[Fe^{\cdots}][I^-]}{1 + \frac{k_2}{k_3}\frac{[Fe^{\cdot\cdot}]}{[Fe^{\cdots}]}}$$

Since the constant of the dark equilibrium is given by the mass action law

$$(2) \quad K = \frac{[Fe^{\cdots}][I^-]}{[Fe^{\cdot\cdot}]^2[I_2]}$$

it is obvious, that the reverse reaction—the thermal reduction of iodine—must follow a similar equation, as that for oxidation of iodide ion. Wagner pointed to the analogy between these expressions and the equation for the rate of thermal formation of hydrogen bromide, obtained by Bodenstein and Lind,[95] and suggested accordingly that also in the reactions of iodine and iron ions an intermediary product is formed which can react either with ferrous or with ferric ions.

The fourth of the reactions above enumerated: the oxidation of iodide ion by ferric ion under the action of light is apparently non-existent, since Rideal and Williams demonstrated that light does not cause either an acceleration, or retardation of iodine formation by ferric ion, provided the concentration of iodine formed is kept low by means of added sodium thiosulfate. The remaining three processes lead to an equation for the rate of total reaction on illumination which is highly inconvenient for practical calculations of the (pure) photochemical reaction rate. Rideal and Williams obtained this last value by noticing that, on illumination, the rate of change of iodine titer (from the thermal equilibrium value) can be approximately represented by a unimolecular reaction equation. Calculating by means of the formula

$$kt = ln \frac{[I_2]_{equil.}}{[I_2]_{equil.} - [I_2]_t}$$

the rate of reaction in the initial stages of illumination of the thermal equilibrium solution, when the dark reactions compensate each other

[93] Sasaki, *loc. cit.*; Schükarew, *Z. physik. Chem.*, 38, 353 (1907). Banerji and Dhar, *Z. anorg. Chem.*, 134, 172 (1924).
[94] *Z. physik. Chem.*, 113, 261 (1924).
[95] *Ibid.*, 57, 108 (1906).

Rideal and Williams found that one molecule of iodine reacted per absorbed light quantum (5790 Å.). They suggested also that the rate of photochemical reaction is independent of the concentrations of reactants, being fully determined by the amount of absorbed light energy. On the other hand, the rate of thermal ionic reactions is dependent, according to modern theories,* not only on the concentrations of the reactants but also on their activity coefficients. An increase of these latter will increase the rate of thermal reactions, but will leave unchanged the rate of the photochemical, according to the equivalence law. The effect resulting will be that the position of the photochemical stationary state, in which the dark and light reactions must balance each other, will be shifted towards the dark equilibrium position. Such an effect was actually observed by Rideal and Williams on making the solution 1.5 normal with respect to potassium chloride. The measurements of the temperature coefficient of the photochemical reaction by Rideal and Williams indicate a value somewhat less than 1.17. Since the free iodine is practically completely converted to the light absorbing triodide ion I_3^- in solutions with excess of potassium iodide, Rideal and Williams concluded that the photochemical reaction is represented by the equation:

$$2Fe^{\cdot\cdot} + I_3^- + h\nu \rightarrow 2Fe^{\cdot\cdot\cdot} + 3I^-.$$

They claimed further that the reaction shows a pronounced maximum of sensitivity for the spectral region 6500-5500 Å. and connected this maximum with the known critical potential of the iodine molecule (2.34 *V.*) which corresponds to the wave length 5300 Å.

This maximum of sensitivity is, however, highly improbable, since the triodide ion is known to have a steadily increasing light absorption coefficient from the red into the ultraviolet.

Accordingly, Kistiakowsky [96] repeated the experiments of Rideal and Williams and found the same quantum yield of unity for the following wave lengths: 5790; 5460; 4360; 3660 Å. Evidently no relation to the critical potential, 2.34 volts, can be established, since the quantum energy (expressed in terms of electron energy) varies from 1.9 to 3.4 volts, but the quantum yield remains unchanged. It was demonstrated by Dymond [97] that gaseous iodine is dissociated into atoms only on absorption of radiation of shorter wave length than 5000 Å., and that an excited and a normal atom are the result of this process. To assume a similar behaviour of the triodide ion without

* See Chapter V.
[96] *J. Am. Chem. Soc.*, 49, 976 (1927).
[97] *Z. Physik.*, 34, 553 (1925).

further study seems to be unjustifiable [98] and, therefore, both the following reaction mechanisms appear possible at present:

$$\text{I.}\quad I_3^- + h\nu \rightarrow I^- + 2I \qquad I + Fe^{\cdot\cdot} \rightarrow I^- + Fe^{\cdot\cdot\cdot}$$

$$\text{or}$$

$$\text{II.}\quad I_3^- + h\nu \rightarrow I_3^- \text{ (activated)} \qquad I_3^- \text{ act.} + Fe^{\cdot\cdot} \rightarrow 2I^- + Fe^{\cdot\cdot\cdot} + I \qquad I + Fe^{\cdot\cdot} \rightarrow I^- + Fe^{\cdot\cdot\cdot}$$

Further indications as to the actual mechanism of this reaction will be discussed in a subsequent chapter.

The success of the application of the equivalence law to the two reactions described possesses a general importance, since it shows that no difficulties in principle exist in treating the real (as contrasted with the ideal treated by Einstein) photochemical stationary states from the point of view of quantum laws. Of course the reactions of nitrosyl chloride and of iodine offer particularly simple kinetic relations.

The Polymerisation of Anthracene. More complicated are the kinetics of the polymerisation of anthracene under the action of light. This reaction has been the object of extensive studies by Luther and Weigert [99] and Weigert.[100] The authors observed that, in ultraviolet light, the reaction

$$2C_{10}H_{14} \rightarrow C_{20}H_{28}$$

proceeds independently of the state of anthracene (solid, vaporised or dissolved). In the more quantitative experiments, however, only solutions of anthracene in boiling organic solvents were investigated. It was found that, on increasing the time of illumination, a stationary state can be reached, the concentration of dianthracene in solution being then directly proportional to the intensity of light and decreasing rapidly with increasing temperature (to 0.34 of the former value for 10° temperature increase). The same stationary state can be reached when the original substance is a solution of dianthracene.

The study of the separate processes revealed that the depolymerisation is a unimolecular thermal reaction, which has a high temperature coefficient (2.8). The rate of polymerisation in light, when studied at lower temperatures, was found to be a reaction of zero order approximately, only slightly affected by temperature (temp. coeff. 1.1 in phenetole). The zero order of photochemical reaction indicated that the absorption of active light is more or less complete. Luther and Weigert, placing between the reaction vessel and the light source, light filters of anthracene solutions, found that, actually, the active ultraviolet radiation is completely absorbed by solutions

[98] Comp. Berthoud and Bellenot, *Helv. chim. Acta*, 7, 307 (1923).
[99] *Z. physik. Chem.*, 51, 297 (1905); 53, 385 (1905).
[100] *Ber.*, 42, 850 (1909).

of anthracene even in layers only a few mm. thick. The rate of photochemical reaction is thus apparently proportional to the amount of light energy absorbed.

Combining Luther and Weigert's observations on the rates of thermal and photochemical reactions we find that the rate of dianthracene formation is given by the following equation:

$$(1) \quad + \frac{d\,[\mathrm{D}]}{dt} = I_0 k_1 - k_2\,[\mathrm{D}]$$

in which [D] represents the concentration of dianthracene and I_0 the intensity of incident light. Accordingly, in the stationary state, the concentration of the polymer will be:

$$(2) \quad [\mathrm{D}] = \frac{I_0 k_1}{k_2} . = I_0 K.$$

This relation indicates that the stationary concentration will be proportional to the light intensity and will decrease with increasing temperature as was actually found. A more exact investigation revealed however that K of equation (2) is also slightly dependent on the anthracene concentration:

TABLE 13.

Anthr. mols per liter.....	0.010	0.020	0.040	0.080	0.120	0.160	0.240	0.300
$K \times 10^3$	(2.31)	2.85	3.55	4.85	5.60	5.65	5.98	5.95
$K \times 10^3$ calcul.	1.87	2.85	3.86	4.67	5.06	5.27	5.45	5.60

This increase of the constant with anthracene concentration was found to be due not to the variation of the dark velocity constant k_2, but to the increase of the rate of dimerisation (approaching a limiting value) at higher concentrations of anthracene. Although the absorption of active radiation was found to be complete even in dilute solutions of anthracene, it was still possible that in these solutions a part of the light is absorbed by the solvent (phenetole at about 160°) or by the polymer according to the equation (see page 39):

$$I_{\text{anthrac.}} = I_{\text{total}} \frac{\alpha_A c_A}{\alpha_A c_A + \alpha_D c_D + \alpha_s c_{\text{solvent}}}$$

and is thus lost for the photochemical change. Experiments carried out with solutions of anthracene screened by pure solvent or by dianthracene solutions demonstrated, however, that α_D and α_S are so small that this cause can account for only 12 per cent increase in the stationary constant K when the anthracene concentration is being changed from 0.01 to 0.3N. Another complication of the reaction kinetics is the observed variation of the rate of photochemical re-

action in different solvents, this rate decreasing from toluene to xylene, benzene, anisole and phenetole. Concentrations of anthracene employed for these experiments were from 0.04 to 0.09*N*, and the velocity constant in different solvents was found to vary in the ratio 1:1.8. This ratio, however, is only approximate, since the experiments in different solvents were not carried out at the same temperature and the temperature coefficient of the photochemical reaction rate was measured only in phenetole (1.1).[101]

Luther and Weigert, in order to explain the observed increase of the velocity constants in more concentrated solutions, suggested the formation of some intermediary products and, ascribing to them certain properties, arrived at equations representing fairly well their experimental results. Byk [102] and Weigert [103] advanced later entirely different theories of this reaction based on somewhat doubtful considerations of classical thermodynamics. Their developments have now very little, except historical, interest and will not be discussed here. Instead, the attempt will be made to arrive, on the basis of the quantum theory of light absorption, at a reaction mechanism which seems at present to be in fairly good agreement with the experiments of Luther and Weigert and does not involve many assumptions as to the properties of intermediary products. The photochemical dimerisation of anthracene is rather promising for such theoretical treatment since, according to Bodenstein's estimate,[104] the quantum yield in experiments of Luther and Weigert was of the order of unity. Later experiments of Weigert [105] allow an independent and more exact estimation. Bodenstein used them to calculate a value of approximately 0.3 molecules of anthracene per quantum of light absorbed. Another useful fact for a theory of anthracene dimerisation is that anthracene emits fluorescence under the action of ultraviolet light. Its absorption spectrum was recently studied in detail by Hyatt [106] who found a number of absorption bands, the most prominent of which have maxima at about 3800, 3600, 3400, 3260 Å. All these bands are responsible for the photosensitivity of anthracene and at the same time for its fluorescence.[107] According to Luther and Weigert, the photochemical reaction rate is slightly dependent on the solvent; their experiments, however, were carried out with dilute solutions

[101] Later experiments of Weigert (*loc. cit.*) indicate that the temperature coefficient is smaller, very near to unity.
[102] *Z. physik. Chem.*, 62, 454 (1908).
[103] *Ibid.*, 63, 458 (1908).
[104] *Loc. cit.*, p. 18.
[105] *Ber.*, 42, 850 (1909).
[106] *Phys. Rev.*, 19, 391 (1922).
[107] Capper and Marsh, *J. Am. Chem. Soc.*, 47, 2847 (1925).

of anthracene only. If, on the other hand, the "apparent order" of the reaction or the increase of the velocity constant for the concentration interval 0.04-0.09 N, be compared, we find that, in toluene, the order is 0.20, in benzene 0.32, in xylene 0.26 and in phenetole and anisole about 0.40. The calculated order is evidently lower for those solvents in which, at the low concentration 0.04 N, a higher rate of reaction was observed, as if the action of the solvents consisted not in the change of the limiting value for high anthracene concentrations but mainly in a more or less rapid attainment of this value at relatively low concentrations. In order to arrive to a kinetic equation representing the rate of polymerisation of anthracene we will assume, as did Luther and Weigert and later Bodenstein, that, on absorption of light energy by anthracene, excited molecules are formed. These then either emit the absorbed energy as fluorescence or react on collision with another anthracene molecule:

$$\begin{array}{lll} (1) & A + h\nu \rightarrow A' & (k_1) \\ (2) & A' \rightarrow A + h\nu' & (k_2) \\ (3) & A' + A \rightarrow A_2 = D & (k_3) \end{array}$$

The rate of formation of the excited anthracene molecules will be expressed by:

$$(4) \quad + \frac{d\,[A']}{dt} = I_{abs.}\, k_1$$

their rate of destruction by:

$$(5) \quad - \frac{d\,[A']}{dt} = k_2\,[A'] + k_3\,[A']\,[A]$$

We will further assume that under steady illumination the concentration of the excited molecules becomes constant:

$$+ \frac{d\,[A']}{dt} = - \frac{d\,[A']}{dt} \text{ and}$$

$$(6) \quad I_{abs.}\, k_1 = k_2\,[A'] + k_3\,[A']\,[A];$$

$$[A'] = \frac{I_{abs.}\, k_1}{k_2 + k_3[A]}$$

The rate of formation of dianthracene is then given by:

$$(7) \quad + \frac{d\,[D]}{dt} = k_3\,[A']\,[A] = I_{abs.} \frac{k_1\, k_3\,[A]}{k_3\,[A] + k_2} = I_{abs.} \frac{k_1\,[A]}{[A] + \frac{k_2}{k_3}}$$

When the stationary state of the reaction is reached, the rate of photochemical formation of dianthracene must be equal to the rate of (dark) depolymerisation, or

$$(8) \quad + \frac{d\,[D]}{dt} = k_4\,[D]$$

and the stationary concentration of dianthracene is therefore given by

$$(9) \quad [D] = I_{abs.} \frac{k_1}{k_4} \frac{[A]}{[A] + \frac{k_2}{k_3}}$$

How far this equation is in agreement with the experimental results will be seen from Table 13, where, under $K_{calc.}$, the calculated values are represented. The equation (7) shows that the concentration range at which the limiting reaction velocity is attained, as also the reaction velocity at lower concentrations of anthracene, are determined by the ratio $\frac{k_2}{k_3}$. This ratio, if the reaction mechanism is correct, must be influenced by the nature of the solvent according to the experiments of Luther and Weigert. Some independent evidence in favour of such influence can be obtained from the experiments of Wawiloff [108] on extinction of fluorescence of dye solutions. A decrease of the fluorescence intensity was observed at higher dye concentrations and was interpreted by Wawiloff as due to occurrence of inelastic collisions between excited and normal dye molecules. Wawiloff found also that the concentration range at which this effect took place was considerably influenced by the solvents studied. From this he deduced that the solvents must influence the ratio of the velocity constants of the two competitive processes: the loss of energy on collisions and the emission of fluorescence. The parallelism is rather close between these processes and those which we assumed to take place in the photochemical reaction of anthracene. It should be noted, however, that identical results with respect to the equation representing the rate of reaction will be obtained if, instead of assuming the re-emission of light as fluorescence by excited anthracene molecules, the loss of excitation energy is assumed to occur by inelastic collisions with the solvent molecules. Of course only a simultaneous study of the rate of reaction and of the intensity of fluorescence in solutions of different concentrations of anthracene can decide between these two suggested variations of the reaction mechanism.

As was shown by Volmer and Riggert [109], a different primary effect is observed if anthracene solutions are illuminated by extreme ultraviolet light (1800-2000 Å.). The large energy of the quanta of this spectral region is apparently sufficient to detach an electron from the anthracene molecules and not merely to raise it to a higher quantum state—the probable effect of smaller quanta—and thus form excited

[108] *Z. Physik*, 31, 750 (1925).
[109] *Z. physik. Chem.*, 100, 502 (1922).

molecules. The photoelectric effect studied by Volmer and Riggert in hexane solutions does not show the complications observed in the polymerisation reaction and is dependent only on the amount of light energy absorbed.

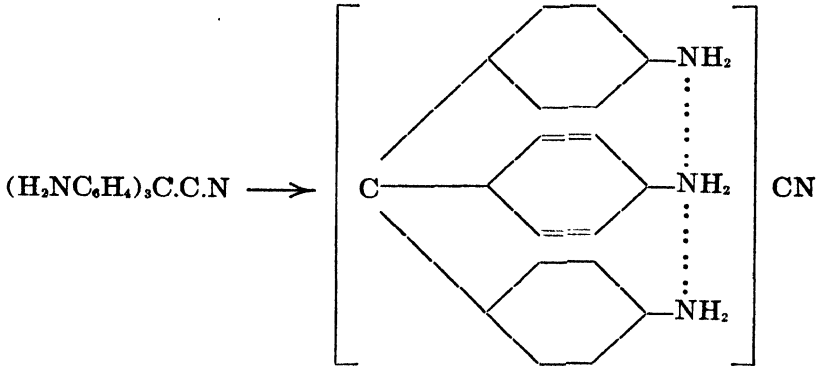
Polymerisation of β-methylanthracene. Weigert and Krüger [110] have studied in detail photochemical polymerisation of β-methylanthracene, this reaction being discovered by Orndorff and Megraw.[111] The results obtained indicate relations so similar to those observed by Luther and Weigert in the polymerisation of anthracene that a detailed discussion appears unnecessary. The effect of solvents on the photochemical rate of polymerisation of the methyl derivative was found, however, to be negligibly small. Also temperature, at least in the more concentrated solutions, does not influence the rate of reaction appreciably. The temperature coefficient is somewhat larger in dilute solutions, although the effect is rather small and not very certain. Weigert and Krüger estimated that the quantum yield of β-methylanthracene polymerisation is some 25 per cent larger than that of anthracene. They assumed, however, that the absorption of light is identical with both substances, an assumption which needs further experimental verification. What is important is that the quantum yields of both reactions are *essentially* the same.

We have discussed so far the few photochemical stationary states which seem to be more or less thoroughly studied, and in which the opposed light and dark reactions could either be separated, or at least their nature indicated by special kinetic studies. Besides these, a large number of photochemical reactions is known, which lead to a stationary state, the opposed reaction being apparently not influenced by light. The great majority of these reactions have been studied only qualitatively and only in a few cases have the kinetics been the object of investigation.

Photo-Isomerism in the Triphenyl Methane Series. Of these we shall mention only an interesting case studied by Lifschitz [112] and by Lifschitz and Joffe [113] of photoisomerisation of the triphenylmethane derivatives, especially of leucocyanides of several dyestuffs. Under the influence of the near ultraviolet the colourless solutions of leucocyanides become coloured and the electrical conductivity of the solutions is increased. The authors suggest that ionised salts of the

[110] *Z. physik. Chem.*, 85, 579 (1913).
[111] *J. Am. Chem. Soc.*, 22, 152 (1899).
[112] *Ber.*, 52, 1919 (1919).
[113] *Z. physik. Chem.*, 97, 426 (1921).

dyestuff bases are formed, the reaction being in general of the same type as represented here for a particular case:



The salts formed decompose thermally, so that under illumination a stationary state is reached, the relative concentrations of the photo products of the reactions being individual for different substances. The solvent shows a very marked influence, almost no reaction occurring in aqueous acid solutions. The addition of cyanide salts of potassium and sodium decreases considerably the stationary concentration of the dyestuff salts formed. The effect of solvents is correlated by the authors with the changes in the absorption spectrum of the leucocyanides, very weak absorption of the ultraviolet being observed in aqueous solutions and strong absorption in alcohol. The action of cyanides consists mainly in the increase of the rate of the opposed dark reaction, a shift in the stationary concentration thus resulting.

Phototropic Changes. Belonging to a certain extent to the class of the light-dark stationary states is a group of particular photochemical processes known as phototropic changes.[114] Apparently no chemical change detectable by ordinary analytical methods is involved in these processes. Instead, under the action of light the absorption spectrum—which means the colour—of "phototropic" substances is changed, the normal absorption bands returning in the dark at a rate which is mainly determined by temperature. Stobbe,[115] however, described a few cases in which both opposed colour changes are influenced by light. Phototropic changes are characteristic of the crystalline state of matter and only few similar reactions in solutions have been described.[116] Experiments of Stobbe [117] demonstrated that phototropic changes are not always entirely reversible. Thus, the

[114] Marckwald, *Z. physik. Chem.*, 30, 143 (1899).
[115] *J. Chem. Soc.*, 123, 2273 (1923).
[116] Comp. for example, Foresti, *Atti accad. Lincei*, 23, II, 270 (1914).
[117] *Lieb. Ann.*, 359, 1 (1908).

colour changes of triphenylfulgide become less and less pronounced on repeated exposures to light. Normally, the absorption bands of a phototropic substance are shifted on illumination towards higher wave lengths; thus, yellow substances become orange-red and colourless substances become violet-red on illumination.[118] Organic and even inorganic [119] chemistry furnish an extraordinary variety of substances showing the phototropic effects, but, so far, little is known as to the relations between the property of reversibly changing colour on illumination and chemical constitution.

Stobbe [120] demonstrated that in the group of fulgides:

$$\begin{array}{l} R.R'.C = C - C{=}O \\ \qquad\quad | \qquad\quad >O \\ R''.R'''.C = C - C{=}O \end{array}$$

only those show phototropism, in which one or two R radicals are hydrogen atoms. Padoa and Santi [121] showed that osazones:

$$\begin{array}{l} R'.R''.N - N = C - R''' \\ \qquad\qquad\quad\ | \\ R'.R''.N - N = C - R''' \end{array}$$

which are wholly substituted are also not phototropic. Graziani [122] studied the phototropism of substituted hydrazones:

$$X{-}C_6H_4{-}NHN{=}CH{-}R$$

where X denotes a halogen atom. Apparently a m-position of the latter is particularly favourable for a marked phototrophy of these substances. On the other hand, Gallagher [123] affirms that no definite relations between chemical constitution and phototropism can be detected.

The kinetics of the process have been the object of a series of investigations by Padoa and his co-workers. He demonstrated [124] that the transformations of solid saliciliden β-naphthylamine and of benzaldehyde-phenylhydrazone in light follow the equation of a unimolecular reaction and that the thermal reverse transformation is a bimolecular process. The temperature coefficient of many phototropic changes [125] is of the order usually observed in photochemical reactions (1.03-1.40), whereas the reverse transformation of the light modification is more sensitive to temperature and has values typical for thermal reactions (2.0 and more).

[118] Stobbe, *loc. cit.*
[119] Mourelo, *Chem. News*, 120, 289 (1920).
Singh, *Quart. J. Indian Chem. Soc.*, 1, 45 (1924).
[120] *Loc. cit.*
[121] *Atti accad. Lincei*, 22, II, 504 (1913).
[122] *Gazz. chim. ital.*, 43, II, 536; 674 (1913).
[123] *Bull. Soc. Chim. France*, 29, 261 (1921).
[124] *Atti accad. Lincei*, 22, II, 500 (1913).
[125] Padoa and Tabellini, *Atti accad. Lincei*, 21, II, 188 (1912).
Padoa and Foresti, *ibid.*, 22, II, 576 (1913).

As a result of his studies Padoa put forward the view that phototropic changes are depolymerisations represented by the equation

$$A_2 \underset{\text{dark}}{\overset{\text{light}}{\rightleftarrows}} 2A.$$

Besides this scheme, polymorphism, stereoisomerism, isomerism and intramolecular changes have been occasionally suggested as causes of phototropism, but apparently the application of these theories to the experimental material met with difficulties.

Weigert [126] studied the colourless β-tetrachloride-α ketonaphthalene with respect to phototropic properties. These were found to be restricted to the crystalline state and be dependent on the direction of the light beam relative to the crystal axes. However, no proportionality between the absorption of active ultraviolet rays and phototropic change at different orientations of the crystals was found. The reverse transformation of the violet modification formed on illumination with ultraviolet light is accelerated not only by higher temperature but also by the visible light absorbed by it. Weigert suggests that a mechanical shift of atoms or molecules in the crystal lattice under the action of light is the cause of phototropism.

Gallagher [127] compared the phototropic and photoelectric properties of different substances and found no parallelism. He suggests that a phototropic change consists in a distortion of electronic orbits in light absorbing molecules, or that electrons are raised to higher quantum states. Singh [128], on investigation of phototropic changes in solutions, suggested that they are related with the presence of keto and enol isomers of dissolved molecules, and that, under the action of light, a quinhydrone group is being formed.

Reviewing the experimental results discovered and the theories advanced to account for phototropism, we must come to the conclusion that the cause of this effect is probably not the same for different classes of chemical compounds and that, therefore, a single theory will be hardly able to account for all the observations made in this field.

Before starting to discuss another type of stationary states in which both opposed reactions acquire a measurable speed under experimental conditions only by the action of light, it seems apposite to remark that, if our knowledge of the light-dark stationary states is by no means complete, our knowledge of the kinetic mechanism of

[126] *Z. Elektrochem.*, 24, 222 (1918).
[127] *Bull. Soc. Chim. France*, 29, 261 (1921).
[128] *Quart. J. Indian Chem. Soc.*, 1, 45 (1924).

the reactions belonging to the second group of (purely photochemical) stationary states is still less. It seems to be almost impossible, from the available experimental results, most of which are of earlier data, to arrive at definitive conclusions concerning the mechanism of the different reactions belonging to this class. Their inclusion in this chapter does not imply that they are expected to follow the equivalence law. The complicated kinetic relations of some of them indicate rather that the exothermic processes involved in the stationary states belong to the chain reactions, but the lack of kinetic measurements makes a successful treatment from this point of view rather improbable at present. Therefore, a brief account of the observed relations will be given in the subsequent pages.

Our knowledge of these reactions would be greatly advanced if they were studied in monochromatic light and, in this way, inasmuch as different spectral regions are often involved in opposed processes, the kinetics of both separated. But, even when the absorption spectra of the reactants overlap each other to a greater extent, the use of monochromatic light in kinetic experiments is very advantageous, since it permits an exact calculation (see equation p. 39) of the amounts of light energy causing each of the opposed reactions.

Stationary State with Maleic and Fumaric Acids. The studies of Warburg on the rate of isomerisation of maleic and fumaric acids, each in the absence of the other acid, have already been recorded. Here is a case in which both substances absorb light of the same spectral region and therefore, even in monochromatic light, the result of longer illumination must be a stationary state. Warburg actually calculated the stationary concentrations of both acids, using the measured light absorption coefficients and the quantum yields of both substances. He arrived at figures which are very close to the values obtained by Kailan [129] on illumination of the acids in solution by the total radiation of a mercury lamp: 75-79 per cent of maleic and 25-27 per cent of fumaric acid. The good agreement between Warburg's calculation and Kailan's experiments indicates that the quantum yield of both reactions is either not affected at all or (less probably) that both are affected in the same way by the presence, in the illuminated solution, of the other acid.

Stationary State with Sulfuryl Chloride. Monochromatic light was also used in the experiments of LeBlanc, Andrich and Kangro [130] on the reactions of sulfuryl chloride. According to these authors, the

[129] *Z. physik. Chem.*, 87, 333 (1914).
[130] *Z. Elektrochem.*, 25, 229 (1919).

absorption spectra of chlorine, sulfur dioxide and sulfuryl chloride show strong maxima of absorption in different spectral regions of the ultraviolet. That of chlorine is situated in the near ultraviolet, of sulfur dioxide at about 3000 Å. and that of sulfuryl chloride below 2500 Å. This circumstance makes possible a separate study of the reactions caused by absorption of light by only one of the components of the mixture $Cl_2 + SO_2 + SO_2Cl_2$ if (approximately) monochromatic light be used. The authors actually found that short ultraviolet absorbed by sulfuryl chloride caused its quantitative decomposition. The rate of reaction is approximately of zero order, in agreement with the observed strong absorption of effective rays by sulfuryl chloride, and is unaffected by the products of decomposition. On the other hand an illumination of a sulfur dioxide-chlorine mixture by light of the 3000 Å. region caused a slow decomposition of sulfur dioxide with formation of molecular sulfur and apparently no other reaction. When, however, the total radiation of a mercury lamp was used, the most intensive lines of which are strongly absorbed by chlorine, completely different relations were obtained. The decomposition of sulfuryl chloride showed a marked autocatalytic effect and was not complete, a stationary state being reached after several hours of illumination. Mixtures of chlorine and sulfur dioxide were found to combine to sulfuryl chloride, under action of light absorbed by the former, the same stationary state as in experiments with sulfuryl chloride being finally reached.

These observations indicate that chlorine not only combines with sulfur dioxide but also photosensitizes the decomposition of sulfuryl chloride. The photochemical stationary concentration of this latter is much higher than in the thermal equilibrium [131] and was found to decrease rapidly with temperature increase. Inasmuch as earlier observations of Trautz (*loc. cit.*) indicated that the rate of sulfuryl chloride formation is only slightly affected by temperature (Trautz found a negative temperature coefficient: 0.88 for 10°), the rate of photosensitised decomposition must have a rather high temperature coefficient. The kinetics of the partial processes going on in the mixture of chlorine, sulfur dioxide and sulfuryl chloride were not studied quantitatively by LeBlanc. His experimental data indicate rather that the rate of sulfuryl chloride formation is represented by the equation

$$+\frac{d\,[SO_2Cl_2]}{dt} = k\,[Cl_2]$$

[131] Trautz, *Z. Elektrochem.*, 21, 336 (1915).

However, Trautz found that, at least at about 100° C., the rate of this reaction is better represented by the equation:

$$+\frac{d\,[SO_2Cl_2]}{dt} = k\,[Cl_2]\,[SO_2]$$

The reaction mechanism is undoubtedly complicated, since LeBlanc and his co-workers observed that moisture accelerates the rate of sulfuryl chloride formation.

Later, Tramm [132] demonstrated that pure and thoroughly dried sulfur dioxide and chlorine do not combine at all under the influence of light. Bonhoeffer [133] measured the quantum yield of sulfuryl chloride formation and obtained values of the order of unity. His experimental arrangement indicates that noticeable amounts of moisture were present in the reacting gases. LeBlanc and co-workers found, in agreement with earlier observations of Trautz, that sulfuryl chloride is not the only product of the chlorine-sulfur dioxide interaction in light. Some other substance of higher boiling point must have also been formed in small quantities.

Stationary State with Hydrogen Halides. The experiments of Coehn and Stuckard on the decomposition and formation of hydrogen halides in light have already been discussed. In general, a stationary state (at 270°) was reached in their experiments, which depended on the wave lengths transmitted by the walls of the reaction vessels (quartz, uviol glass, ordinary glass). As light source, the total radiation of a mercury lamp was used. Although the partial processes leading to the stationary states have since been the object of several, more quantitative investigations, the results of Coehn and Stuckart, represented in Table 14, are still of some interest. The decrease of percentage decomposition in the direction iodide-bromide-chloride is well in accord with the known shift of the absorption spectrum of these halides towards the extreme ultraviolet and with the increasing

TABLE 14.

Halide	HI	HBr	HCl
Wave length transmitted	Degree of decomposition (stationary state)		
>2000Å.	92 per cent	100 per cent	0.42 per cent
>2500Å.	100 "	80 "	0.0 "
>3000Å.	100 "	0 "	0.0 "

rate of formation of halides in light. Coehn and Stuckard demonstrated further, using different concentrations of hydrogen and iodine,

[132] *Z. physik. Chem.*, 105, 356 (1923).
[133] *Z. Physik*, 13, 94 (1923).

that the concentration of hydrogen iodide in the stationary state does not follow the mass action law. The quantitative measurements of Warburg of the quantum yield in bromide and iodide decomposition have already been discussed. Tramm [134] demonstrated that the rate of these reactions is not affected by thorough drying, but that the decomposition of pure hydrogen chloride in extreme ultraviolet light does not take place if the gas is thoroughly dried. Apparently the suggestions of Warburg already discussed on the mechanism of hydrogen halide decomposition cannot be applied directly to hydrogen chloride.

Stationary State with Water Vapour. A deviation from the mass action law was observed by Coehn and Grote [135] and by Andrejew,[136] who studied the action of ultraviolet light on water vapour and on mixtures of oxygen and hydrogen. Longer illumination of these substances leads to a stationary state in which the concentration of hydrogen and oxygen was found to be independent of the pressure of water vapour over a wide range. Studying the rate of water formation, Andrejew obtained a reaction of zero order; Coehn and Grote, on the other hand, an approximately unimolecular reaction. These results are possibly not contradictory since the "order" of reaction is dependent on the degree of absorption of active radiation by oxygen and actually both investigators used differently shaped reaction vessels and different concentrations of the gases. The rate of water formation is, however, undoubtedly not of zero order when only very small quantities of oxygen are present—as in the stationary state of water decomposition. This conclusion, combined with the experimentally determined zero order of the rate of water decomposition, leads, as was demonstrated by Bodenstein,[137] to the observed invariability of stationary concentration of water decomposition products. The primary interaction of illuminated oxygen and hydrogen probably results in the formation not of water but of hydrogen peroxide. At least Tian [138] succeeded in isolating appreciable amounts of this latter on short illumination and suggested that formation of water is due to a secondary decomposition of hydrogen peroxide in ultraviolet light.

According to Coehn and Tramm,[139] an initial drying of the gases does not affect the rate of water formation. This result is disputed

[134] *Z. physik. Chem.*, 105, 356 (1923).
[135] Nernst, "Festschrift" (1912).
[136] *J. Russ. Chem. Soc.*, 43, 1342 (1911); *Z. Elektrochem.*, 19, 551 (1913).
[137] *Z. physik. Chem.*, 85, 357 (1913).
[138] *Compt. rend.*, 152, 1012 (1911).
[139] *Z. physik. Chem.*, 105, 356 (1923)..

by Baker and Carlton,[140] who find water vapour to be a positive catalyst.

Stationary State with Carbon Dioxide. Coehn and Sieper[141] studied the decomposition of carbon dioxide in extreme ultraviolet light (< 2200 Å.). They find that a stationary state can be reached which is largely dependent on the presence of moisture. In dry carbon dioxide circa 18 per cent are decomposed to carbon monoxide and oxygen, whereas in moist gases the stationary state is reached already after decomposition of only 0.1 per cent. These experiments confirm the earlier observations of Chapman, Chadwick and Ramsbottom.[142] Coehn and Tramm,[143] and Tramm[144] found that water has no effect on the rate of carbon dioxide formation from carbon monoxide and oxygen in ultraviolet light. Evidently the change of stationary concentrations in Coehn and Sieper's experiments must be ascribed to a retarding action of water vapour on the rate of carbon dioxide decomposition. Tramm further demonstrated that sulfur dioxide has the same retarding effect as water.

The question of the effect of light on a carbon dioxide-water mixture, important for the problem of assimilation of the former by green plants, has been the object of a series of investigations. Usher and Priestly[145] and Moore and Webster[146] observed a formation of small quantities of formaldehyde in ultraviolet light. Baly, Heilbron and Barker[147] not only confirmed these earlier observations, but also claimed that, in presence of the dye malachite green, formaldehyde is formed in an aqueous solution of carbon dioxide even under the influence of visible light. This last observation was criticised by Baur and Büchi,[148] who suggested that formaldehyde originated from the decomposition products of the dye studied.

Recently, Porter and Ramsperger[149] came to the conclusion, repeating carefully the earlier experiments, that also in ultraviolet light no formaldehyde is formed from a carbon dioxide-water mixture. The different observations of other investigators are apparently due to a contamination of reacting gases by organic matter from stopcock grease, and other organic impurities.

[140] *J. Chem. Soc.*, 127, 1990 (1925).
[141] *Z. physik. Chem.*, 91, 347 (1916)
[142] *J. Chem. Soc.*, 21, 942 (1907).
[143] *Ber.*, 54, 1148 (1920).
[144] *Loc. cit.*, p. 77.
[145] *Proc. Roy. Soc.*, 84*B*, 101 (1911).
[146] *Ibid.*, 90*B*, 168 (1918).
[147] *J. Chem. Soc.*, 119, 1025 (1921).
[148] *Helv. Chim. Acta*, 6, 959 (1923).

Sulfur Dioxide Decomposition. The action of ultraviolet light on oxides of sulfur has been also frequently studied. Coehn [150] and more recently Hill [151] demonstrated that sulfur dioxide is decomposed by the action of ultraviolet light. Hill suggests that the reaction taking place is:

$$3SO_2 \rightarrow 2SO_3 + S$$

since both these decomposition products could be identified. He found, also, that light of the spectral region 2500-3200 Å. is effective in causing the reaction. This observation is in good agreement with the results of LeBlanc and co-workers,[152] who found the absorption maximum of sulfur dioxide to be situated at about 3000 Å.

Coehn [153] further studied the action of light on a mixture of sulfur dioxide and oxygen. On longer illumination, a stationary state is established which is not influenced by temperature (50°-800°), although the rates of opposed reactions must have an appreciable temperature coefficient, which is evidenced by a more rapid attainment of the stationary state on elevation of temperature. According to Coehn, the constant of the photochemical stationary state calculated by the equation of the mass action law,

$$K = \frac{[SO_2]^2\,[O_2]}{[SO_3]^2},$$

is fairly independent of the varying concentrations of the reactants, but has a much higher value than the constant of the dark equilibrium. Of further interest is Coehn's observation that the rate of sulfur trioxide formation is accelerated by moisture. Supported by rather doubtful experiments, Coehn came to the conclusion that the same spectral region is effective in decomposition and formation of sulfur trioxide. On the other hand, he observed a decrease of the "photochemical equilibrium" constant when the intensity of illumination was reduced by decreasing the current flowing through the mercury lamp. Coehn, and independently Andrejew, observed a similar effect of light intensity also on the stationary state in water decomposition. Some of Andrejew's results are represented in the following table.

TABLE 15.

Watt load of the lamp.....	405.0	438.5	449.5	454.6	469.5	471.2	504.7
Degree of decomposition in per cent	.235	.335	.385	.387	.412	.427	.455

[150] *Z. Elektrochem.*, 13, 545 (1907).
[151] *Trans. Farad. Soc.*, 20, 107 (1924).
[152] *Loc. cit.*, p. 74.
[153] *Z. physik. Chem.*, 70, 88 (1909).

Coehn interpreted these observations by suggesting that the rôle of light in causing the decomposition or the recombination reactions, is different: in the first case light energy is doing chemical work, in the second the action is purely catalytic. Therefore with increase of the amount of light energy available for the chemical work a shift of the stationary concentrations *from* the values of the thermal equilibrium should be expected and is actually observed. This interpretation is, however, hardly reconcilable with the modern ideas on the subject. Inasmuch as the velocity of the spontaneous thermal reactions is practically zero at the temperature of all Coehn's and Andrejew's experiments, the opposed processes in the establishment of the stationary state must be regarded as purely photochemical reactions.

In case the rates of all reactions were proportional to the light intensity the variations of this latter could cause only a more or less rapid attainment, but not an actual change of stationary concentrations. It is thus necessary to assume that some of the partial reactions in both stationary states are not proportional to the light intensity. Another possibility is that, contrary to the statement of Coehn, the decompositions of water or sulfur trioxide are caused by shorter wave lengths than the respective recombination processes and that the intensity of the extreme ultraviolet radiation of a mercury lamp increases more rapidly with increasing load of the lamp than does the intensity of other spectral regions.[154]

The brief account of photochemical stationary states given in the preceding pages has demonstrated the wide variety of observed relations. The evident success of the application of the equivalence law to such stationary states as the reduction of iodine by ferrous ions or the decomposition of nitrosyl chloride would tempt one to apply the same principle in dealing with the kinetics of other reactions of this group, but the relatively very incomplete knowledge of these reactions on the other hand reduces the value of possible calculations of the quantum yield. It is evident that a mere statement that the number of molecules reacting is a certain multiple of the number of quanta absorbed at particular values of concentrations and temperature, has little value for a thorough study of the reaction mechanism, unless the variations of the quantum yield, as a function of concentrations and temperature, are known.

[154] See Pflueger, *Ann. Physik*, 26, 789 (1908).
Coblentz and Kahler, *Bur. Stand. Sci. Paper*, 378.

CHAPTER III

CHAIN REACTIONS

In the first part of the preceding chapter we discussed those photochemical reactions, which, on more thorough study, revealed simple relations between the number of molecules reacting and light energy quanta absorbed. These relations, when combined with a sound treatment of possible secondary processes, led to a full confirmation of the quantum laws of light absorption as applied to photochemically active substances.

In the earlier days of photochemistry a sharp distinction was frequently drawn between processes occurring with increase of the free energy of the system and spontaneous photochemical processes. The experimental reason for this separation lies in the observation that many spontaneous reactions proceed at a rate incomparably faster than all processes opposed to the normal free energy factors. In theoretical discussions of the spontaneous photochemical reactions the opinion was frequently advanced that, in these, the rôle of light is the rôle of a catalyst, since no chemical work is done by the radiant energy. From the point of view of modern photochemistry the classification of light as a catalytic agent is unjustified, unless an extremely broad meaning be given to this last term, a meaning that almost excludes its successful application in the treatment of chemical kinetics. This conclusion can be arrived at from the consideration that only *absorption* of light energy and not the mere presence of light can cause photochemical reactions. According to all experience, this absorbed energy is never re-emitted as isochromatic radiation in the reaction, in contradistinction to material catalysts which emerge unchanged at the end of a catalytic process. Thus, if a classification of light be really needed, one should attribute to light rather the rôle of a reactant than that of a catalyst.

As will be seen from the following, for a successful general treatment of photochemical kinetics a different assumption is very helpful, namely, that the primary action of light is, independent of the thermodynamic character of the total reaction, always essentially the same: activation of, on an average, one molecule (or atom) per absorbed

light energy quantum. Thus, for instance, in both the spontaneous decompositions of chlorine monoxide and hydrogen iodide and in the energy consuming decomposition of hydrogen bromide, the number of molecules reacting is a small multiple of the number of light energy quanta absorbed. We have seen that certain secondary processes had to be introduced into the suggested mechanisms of these reactions in order to account for the quantum yields being equal to two. In some of the spontaneous reactions to be discussed later, the quantum yields are much larger, equal to many thousands. This, however, in no way affects our main assumption, but, obviously, indicates that, in spontaneous reactions, secondary processes may under favourable conditions play a still more important rôle in the balance of the total reaction. This is the only difference between the two classes of photochemical processes. Thermochemistry gives a ready answer to the question why, in endothermic reactions, the number of molecules reacting is strictly limited by the amount of absorbed light energy, whereas in exothermic, under ordinary experimental conditions usually the spontaneous, reactions, the primary products, formed on light absorption, may cause a long sequence, a chain, of secondary chemical processes.

The Hydrogen Chlorine Combination

The reaction of chlorine with hydrogen is often considered the classical example of photochemistry and is becoming the classical chain reaction. It was discovered as early as 1801 [1] and since then has been the object of an extraordinarily large amount of experimental work equalled only by the amount of theoretical speculation devoted to the explanation of the reaction mechanism and, from it, to more general problems of photochemistry. Yet, even now, we do not possess a uniform explanation of all the effects observed, though great progress has been achieved in the last decade.

For the purpose of following the rate of reaction, earlier investigators of the hydrogen-chlorine combination used exclusively an apparatus which contained, besides the gas mixture, a small amount of water. The volume decrease, resulting from solution in water of the hydrogen chloride formed, was used as the indicator of the progress of reaction. Draper [2] was the first to construct an apparatus of this type and to use it for systematic experiments. His deduction of the Grotthuss-Draper photochemical law on the basis of these experi-

[1] Cruickshank, *Nicholson's J.*, 5, 202 (1801).
[2] Draper, *Phil. Mag.*, 19, 195 (1841); 23, 401 (1843); 27, 327 (1845).

ments has already been mentioned. Draper, among other observations on the peculiarities of the hydrogen-chlorine reaction, described a particular initial effect of radiation, namely, that the volume (or pressure) decrease was always preceded by an initial increase of short duration. This, so-called Draper effect, was interpreted by later investigators, as due to a heating of the gases by the absorbed light energy and by the energy liberated in the reaction.

The Induction Period. Another peculiarity of the hydrogen-chlorine reaction was studied in particular by Bunsen and Roscoe.[3] In their experiments, formation of hydrogen chloride did not set in instantaneously on illumination, but was preceded by a period of variable duration with almost no reaction taking place. This induction period, which for a long time was assigned an important rôle in the theoretical development of photochemistry, was found by Bunsen and Roscoe to be dependent not only on the mode of preparation of the gases but also on their former history, being, for instance, greatly shortened by a previous illumination. Since the work of Bunsen and Roscoe, the induction period has been frequently studied. Its nature is now explained, due especially to the researches of Burgess and Chapman [4] and Chapman and MacMahon.[5] These authors proved that the induction period is caused by impurities in the gases used, as well as by impurities on the walls of the containing vessel and in the absorbing liquid. The action of different impurities was found by these authors to be specific, for instance, oxidising agents like nitric acid and hydrogen peroxide did not show it,[6] but ammonia, nitrogen trichloride, chlorine dioxide, and some other substances, among which the organic nitrogen compounds may especially be noted, increased the duration of the induction period enormously. All these substances are probably destroyed or eliminated from the gas phase on illumination, the full rate of hydrogen chloride formation being attained only after this purification has taken place. The time necessary for such removal of impurities determines the duration of the induction period. Chapman and MacMahon suggested, for instance, that ammonia combined with the hydrochloric acid formed and was in this way removed from the gas phase. Recently Norrish [7] objected to this explanation and suggested that a reaction takes place between illuminated chlorine and ammonia, this reaction being localised on

[3] *Pogg. Ann.*, 96 (1855); 100, 101 (1857); 108 (1859).
[4] *J. Chem. Soc.*, 89, 1402 (1906).
[5] *Ibid.*, 97, 845 (1909).
[6] The inactivity of chlorine monoxide and hypochlorous acid was already demonstrated by Mellor, *J. Chem. Soc.*, 81, 1293 (1902).
[7] *J. Chem. Soc.*, 127, 2317 (1925).

the illuminated walls of the containing vessel. His objection to the explanation advanced by Chapman and MacMahon is not incontestable. Norrish pointed out that the rate of hydrogen chloride formation is dependent on the hydrogen concentration and that, if the theory of Chapman and MacMahon were correct, the duration of the induction period caused by ammonia should also be dependent on it. These authors observed, however, that the induction period was not affected by variations in the hydrogen concentration, which indicates, according to Norrish, that their theory is not correct. It is, however, questionable whether the experiments of Chapman and MacMahon can be considered decisive for their theory, since they could easily have overlooked a small influence of hydrogen on the duration of the induction period and, as we shall see, the influence of hydrogen on the rate of hydrogen chloride formation is not large. From theoretical considerations on the mechanism of the chlorine-ammonia reaction, Norrish obtained an equation for the duration of the induction period:

$$T = k_1 [NH_3] \left(1 - \frac{k_2}{[Cl_2]}\right) \frac{V}{S}.$$

The square brackets indicate here the corresponding concentrations and V and S are respectively volume and illuminated surface of the vessel. The experimental results agreed fairly well with this equation, the influence of the surface being studied, however, only qualitatively. The results in this respect are not convincing.

Baly and Barker [8] came to different conclusions concerning the nature of the induction period and suggested that it is an inherent property of the hydrogen-chlorine reaction. Consequently, the authors developed a theory of the reaction based partly on this conclusion. As Weigert [9] pointed out, the results of Baly and Barker's experiments are due probably to the small traces of impurities and cannot be considered convincing.

The Influence of Oxygen. Bunsen and Roscoe had noticed that even the smallest traces of air present in the reaction vessel slowed down the rate of reaction, this action being due to oxygen. Pringsheim [10] suggested that, in the course of the reaction, chlorine monoxide was formed and acted as a retarding agent. This latter, however, is, according to Mellor,[11] incapable of causing an induction period. Burgess and Chapman [12] and Chapman and MacMahon [13]

[8] *J. Chem. Soc.*, 119, 653 (1921).
[9] *Z. physik. Chem.*, 106, 428 (1923).
[10] *Wied. Ann.*, 32, 384 (1887).
[11] *Loc. cit.*
[12] *Loc. cit.*
[13] *Loc. cit.*

showed that the duration of the induction period was independent on the oxygen content, this latter uniformly retarding the rate of reaction. The fundamentally different nature of oxygen action as opposed to those substances producing induction was further demonstrated by Bodenstein and Dux.[14] Their conclusion was that the retarding action of oxygen is proportional to its concentration (in agreement with results of Chapman) and that its active concentration remains apparently constant throughout the course of reaction.

The Kinetics of the Process. Bodenstein and Dux used a distinctly different method in their investigations, avoiding water as absorbing agent, but freezing out both chlorine and hydrogen chloride by means of liquid air. From the residual pressure (of hydrogen and oxygen) the progress of reaction was easily calculable. This method, possessing important advantages over the method usually employed, enabled Bodenstein and Dux to study the rate of reaction at varying concentrations of the components and to follow its whole course and not merely the initial stages.

The results obtained were that the reaction velocity was proportional (in electrolytic gases) to the square of the chlorine concentration, being independent of the hydrogen chloride and hydrogen concentrations. However, with chlorine in large excess of hydrogen, the rate of reaction was also dependent on the concentration of this latter, a good agreement with the experimental results being obtained by the use of the equation

$$\frac{d[HCl]}{dt} = k_1 \frac{[Cl_2]^2 [H_2]}{k_2 + [H]}$$

for the calculation of the velocity constant k_1. Chapman and Whiston[15] came to different results with respect to the influence of the chlorine concentration and suggested that the rate of reaction was proportional to the first power of the chlorine concentration.

The research of Mrs. Chapman,[16] being a repetition and extension of earlier kinetic studies, showed that the rate of reaction was expressible only by a more complicated equation. Her experiments, conducted in an actinometer with water, where only the initial rate of reaction could be observed, indicated that the rate of reaction with widely varying concentrations of single components could be expressed by the following equation

$$\frac{d[HCl]}{dt} = k_1 \frac{[Cl_2]^2 [H_2]}{k_2 [H_2]^{2-x} [O_2] + [Cl_2]}$$

[14] *Z. physik. Chem.*, 85, 297 (1913).
[15] *J. Chem. Soc.*, 115, 1264 (1919).
[16] *Ibid.*, 123, 3062 (1923).

This equation indicates, that the rate of reaction is proportional to a varying power of the chlorine concentration, slightly smaller than the second, is proportional to hydrogen concentration, provided it is small, but is slightly retarded by hydrogen if present in excess. This last result is a confirmation of an early observation by Chapman and Underhill [17] criticised by Bodenstein.[18] The term expressing the joint action of hydrogen and oxygen is important. This term takes account of Mrs. Chapman's observations that, with but little hydrogen present, the rate of reaction becomes almost independent of the oxygen concentration. Mrs. Chapman further found the rate of reaction to be independent of the total pressure in stoichiometric gas mixtures. Quite recently Thon [19] in Bodenstein's laboratory repeated the earlier experiments of Dux using a similar technique. His results, being a full confirmation and a partial extension of Bodenstein's earlier experiments, are in disagreement with observations of Mrs. Chapman, inasmuch as Thon does not find a retarding action with excess hydrogen. Further, Thon finds his experiments to be in a very good agreement with the equation:

$$\frac{d\,[HCl]}{dt} = k_1 \frac{[Cl_2]^2\,[H_2]}{[O_2]\,([H_2]+1/10\,[Cl_2])}$$

which contradicts the result of Mrs. Chapman that oxygen exerts a retarding action only when sufficient hydrogen is present. Of possible importance for a future discussion of the reaction mechanism is the observation of Padoa [20] that iodine exerts a marked catalytic effect on the rate of hydrogen chloride formation.

The Effect of Water Vapour. The catalytic activity of water vapour is still more marked. Early observers had already noticed [21, 22, 23] that the hydrogen-chlorine mixture when thoroughly dried over phosphorus pentoxide reacts only very slowly in light. Bodenstein and Dux,[24] investigating quantitatively the influence of water vapour on the rate of reaction, found no change in reaction velocity when the pressure of water vapour was changed from 0.004 to 2.3 mm. of mercury and concluded that the non-reactivity of gases dried over phosphorus pentoxide might be due to some inhibition. Tramm,[25] however, using the modern vacuum technique and liquid air for freeing both apparatus

[17] *J. Chem. Soc.*, 103, 496 (1913).
[18] *Loc. cit.*
[19] *Z. physik. Chem.*, 124, 327 (1926).
[20] *Gazz. chim. ital.*, 51, I, 193 (1921).
[21] Pringsheim, *Wied. Ann.*, 32, 384 (1887).
[22] Backer, *J. Chem. Soc.*, 65, 611 (1894).
[23] Mellor and Russel, *ibid.*, 81, 1279 (1902).
[24] *Loc. cit.*
[25] *Z. physik. Chem.*, 105, 856 (1923).

and gases from moisture, showed that dry gases did not combine at all in visible light. His experiments were extended by Coehn and Jung [26] to show that, at a pressure of 10^{-7} mm. of water vapour, no reaction occurred even after 20 days' exposure to sunlight. At a pressure of 10^{-5} mm., the reaction rate had already almost attained its normal value, this observation thus confirming Bodenstein's results for higher water vapour pressures.

Under the action of ultraviolet light of shorter wave length than about 3000 Å., even in dry gases containing only 10^{-7} mm. water vapour, a measurable reaction was observed by Coehn and Jung.

Quantum Yield. Bodenstein,[27] comparing the light energy absorbed by chlorine in his experiments and the amount of hydrogen chloride formed, came to the conclusion that as many as 10^6 molecules of chlorine reacted per absorbed quantum. His estimate may be slightly high as Kornfeld and Müller [28] have recently shown that, even with great care in the purification of the gases from oxygen, their quantum yield did not exceed 10^5 molecules.[29] Nevertheless, the main fact, that there is an enormous deviation from the equivalence law, cannot be doubted.

The work of Weigert and Kellerman [30] may be regarded as direct evidence of some sort of chain mechanism. Using an intense spark of very short duration as the source of light, they demonstrated that the reaction did not proceed instantaneously, but required a measurable time for completion. This effect has, however, very little in common with the induction period already discussed, as the time is of a quite different order of magnitude and as this time is longer in more sensitive (pure) gas mixtures. From the observed period of about 0.01 sec. and a calculated quantum yield of about 10^5 molecules, Weigert concluded (assuming a chain reaction to take place) that an atomic process required about 10^{-7} sec. for completion. Especially with respect to this effect of Weigert, it is interesting to note that Bodenstein and Taylor [31] and, more recently, Marshall [32] failed to observe even the slightest reaction when previously illuminated chlorine was led into hydrogen. The time interval between illumination and admixture in the experiments of Marshall did not exceed 3.10^{-4}

[26] *Z. physik. Chem.*, 110, 705 (1924); *Ber.*, 56, 696 (1923).
[27] *Ibid.*, 85, 329 (1913).
[28] *Ibid.*, 117, 242 (1925).
[29] The recent work of Porter, Bardwell and Lind [*J. Am. Chem. Soc.*, 48, 2603 (1926)] indicates reaction yields in excess of this figure.
[30] *Z. Elektrochem.*, 28, 456 (1922); *Z. physik. Chem.*, 107, 1 (1923).
[31] *Z. Elektrochem.*, 22, 202 (1916); comp. also Volmer, *Z. Elektrochem.*, 20, 494 (1914).
[32] *J. Phys. Chem.*, 30, 757 (1926).

sec., oxygen-free chlorine, with and without water vapour, being used.

The Effect of Pressure on Quantum Yield. The observed independence of the rate of reaction of the total pressure of gases [33] is apparently restricted only to higher pressures. Recently, Marshall [34] has shown that, at lower pressures, the quantum yield decreases very rapidly, being, for instance, about 2.10^4 molecules per quantum at 60 mm. and only 20 at 0.01 mm. total pressure. The measurements at these low pressures being extremely difficult, no kinetic study was achieved and the calculated quantum yields must be regarded as approximate. The main fact, however, a thousandfold decrease, is fully established.

Effect of Light Intensity. Draper, and Bunsen and Roscoe found the rate of hydrogen chloride formation to be proportional to the incident light intensity. This proportionality of the reaction rate and light intensity was undisputed until Baly and Barker [35] claimed that the rate increases more rapidly than the light intensity. Thereupon, several investigators [36, 37, 38] repeated these experiments but could not confirm the Baly-Barker observation. The experiments of Kornfeld and Müller especially, in which the light intensity was varied in the ratio 1:64 in a very exact manner, lead to the conclusion that the reaction velocity is strictly proportional to the incident light intensity.

Theories of the Reaction. Following his experimental study with Dux, Bodenstein [39] developed a theory of the process, suggesting that chlorine molecules were ionised by absorption of light and that the expelled electrons caused a chain reaction. Failure to detect ionisation in illuminated chlorine [40, 41, 42] led Bodenstein to propose a reaction mechanism involving activated molecules.[43] Bodenstein suggested that activation consisted, not in high kinetic energy of the molecules, but in a change of electronic orbits, an idea later generalised and applied by Stern and Volmer [44] to all photochemical reactions. Bodenstein further assumed that the deactivation of such active molecules on collision is a specific property of colliding molecules, related to their optical absorption spectra. He suggested, as

[33] Mrs. Chapman, *loc. cit.*
[34] *J. Phys. Chem.*, 29, 1453 (1925).
[35] *J. Chem. Soc.*, 119, 653 (1921).
[36] M. C. C. Chapman, *J. Chem. Soc.*, 125, 152 (1924).
[37] Kornfeld-Müller, *loc. cit.*
[38] Marshall, *J. Phys. Chem.*, 29, 1453 (1925).
[39] *Z. physik. Chem.*, 85, 329 (1913).
[40] Thomson, *Proc. Camb. Phil. Soc.*, 11, 201 (1901).
[41] Kummell, *Z. Elektrochem.*, 17, 490 (1911).
[42] LeBlanc and Volmer, *Z. Elektrochem.*, 20, 494 (1914).
[43] *Z. Elektrochem.*, 22, 53 (1916).
[44] *Loc. cit.*, first chapter.

the sequence of reactions occurring in illuminated hydrogen-chlorine mixture, the following scheme (the activated molecules being here denoted thus: Cl_2'):

$$\begin{aligned}
Cl_2 + h\nu &\rightarrow Cl_2' && (k_1 I_0)\\
Cl_2' + H_2 &\rightarrow 2HCl' && (k_2)\\
HCl' &\rightarrow HCl && (k_3)\\
HCl' + O_2 &\rightarrow HCl + O_2' \rightarrow HCl + O_2 && (k_4)\\
HCl' + Cl_2 &\rightarrow HCl + Cl_2' && (k_5)\\
Cl_2' &\rightarrow Cl_2 && (k_7)\\
Cl_2' + H_2 &\rightarrow 2HCl' && (k_8)
\end{aligned}$$

The activated HCl molecules then repeat the cycle.

The kinetic interpretation of these reactions gives the following equations:

$$\begin{aligned}
+\frac{d[HCl']}{dt} &= I_0 k_1 k_2 [Cl_2] + k_8 [Cl_2'] [H_2]\\
-\frac{d[HCl']}{dt} &= k_3 [HCl'] + k_4 [HCl'] [O_2] + k_5 [HCl'] [Cl_2]\\
+\frac{d[Cl_2']}{dt} &= k_5 [HCl'] [Cl_2]\\
-\frac{d[Cl_2']}{dt} &= k_7 [Cl_2'] + k_8 [Cl_2'] [H_2].
\end{aligned}$$

In order to eliminate the concentrations of (hypothetical) activated molecules from this set of equations, Bodenstein assumed that, almost instantaneously on illumination, a stationary state is reached in the gas mixture in which the concentrations of the active molecules remain constant, the differential quotients on the left of the two pairs of equations thus becoming equal to each other. These two assumptions, that the stationary concentrations of the intermediary reactants are reached within a negligibly small fraction of the observation time and further, that in the subsequent stationary state the concentrations of the intermediary reactants remain constant, have frequently been employed by Bodenstein and others in the theoretical treatment of the kinetics of those photochemical and thermal reactions which do not follow the mass action law as deduced from the stoichiometric equations. The assumptions are thus of general importance to the theory of chemical kinetics; and, since the question may arise as to what extent they are justifiable, it is of some interest to consider them [45] in detail. For this purpose, let us investigate a somewhat simpler reaction scheme than that postulated by Bodenstein:

$$\begin{aligned}
Cl_2 + h\nu &\rightarrow Cl_2' && (k_1)\\
Cl_2' &\rightarrow Cl_2 + h\nu && (k_2)\\
Cl_2' + H_2 &\rightarrow 2HCl && (k_3)
\end{aligned}$$

[45] Comp. Bodenstein, *Ann. Physik*, **82**, 836 (1927). Christiansen, *Z. phys. Chem.*, **128**, 430 (1927).

The rate of Cl_2' formation from the start of illumination will be given by an equation which is easily deducible:

$$1. \quad \frac{d[Cl_2']}{dt} = k_1[Cl_2] - k_2[Cl_2'] - k_3[Cl_2'][H_2]$$

and which, when integrated, yields for the concentration of Cl_2' after a time t has elapsed since the beginning of illumination:

$$2. \quad [Cl_2']_t = \frac{k_1[Cl_2](1-e^{-t(k_2+k_3[H_2])})}{k_2 + k_3[H_2]}$$

In deriving this equation the concentrations of the reactants (H_2 and Cl_2) were assumed to be constant. This is usually a sufficiently close approximation as will be seen from the discussion which follows. Equation 2 shows that the concentration of the activated molecules Cl_2' will become essentially constant soon after the product in the exponent reaches values above unity. The velocity constant k_2 is, in the case of activated molecules and atoms, usually of the order of 10^7 to 10^8 (sec.$^{-1}$) according to spectroscopic observations,[46] and therefore their stationary concentration must practically be reached after time intervals of 10^{-6} to 10^{-7} sec. The second term of the sum in the exponent: $k_3[H_2]$ is of a still higher order of magnitude than the constant k_2, provided a considerable fraction of all collisions between activated molecules and hydrogen result in reaction, and the concentration of the latter is not too small. The result will be a further decrease in the time of attainment of the stationary concentration. The conclusion which can be reached from these considerations is that as long as the mean life—either between activation and deactivation, or between activation and reaction—of the intermediary products is negligibly short in comparison with the observation time, their stationary concentrations can be assumed, for the purpose of kinetic studies, to be established instantaneously on illumination.

The second assumption, that in the stationary state the concentrations of the intermediary reactants remain constant, is undoubtedly not exactly correct. It must be considered, however, that inasmuch as the velocity equations are derived for infinitely short time intervals, the concentrations of all physically existent species, however fast they may be changing, can be assumed to be constant. On the other hand, the non-integrated differential kinetic equations for reactions not in-

[46] Constant k_2 of our scheme is obviously related to the "mean life" of activated molecules, τ, which is the time during which their concentration decreases spontaneously to e^{-1} value, by the expression

$$k_2 = \frac{1}{\tau}.$$

volving intermediary processes, even when applied to experimental data obtained for finite time intervals, give sufficiently close approximations as long as the changes in the concentrations of the reactants are only small fractions of the total. The same degree of approximation should also be obtained for such experimental data from kinetic equations involving intermediary stages, unless the *relative* rate of change of the concentrations of the intermediary products is of a higher order of magnitude than that of the primary reactants. The reverse can easily be demonstrated by means of Equation **2**, which shows that, in the stationary state, the concentration of Cl_2' changes in about the same proportion as the concentrations of the primary reactants. This conclusion can be extended unchanged to more complicated reaction schemes. Generally, therefore, the use of the non-integrated kinetic equations with intermediary processes is limited by the validity of the same assumption as in the case of simple kinetic equations—the constancy of the concentrations of the primary reactants during the time interval studied. The error introduced into the results through the change in concentrations of the intermediary products is only of the same order of magnitude as that due to the approximation first mentioned.

Making the assumptions discussed above it is easy to calculate from Bodenstein's equations the stationary concentration of active chlorine molecules expressed in terms of known concentrations of the reactants. The equation for the rate of hydrogen chloride formation can be obtained by introducing into the equation:

$$-\frac{d[H_2]}{dt} = k_8 [Cl_2'] [H_2],$$

this expression for active chlorine concentration. The resulting equation is:

$$-\frac{d[H_2]}{dt} = I_0 \frac{k_1 k_2 k_5 [Cl_2]^2 [H_2]}{k_4 [H_2] [O_2] + k_3 [H_2] + \frac{k_4 k_7}{k_8} [O_2] + \frac{k_3 k_7}{k_8} [Cl_2] + \frac{k_3 k_7}{k_8}}$$

Neglecting terms in the numerator containing the ratio $\frac{k_7}{k_8}$ an equation will be obtained which is in close agreement with the experimental results of Bodenstein and Dux.

Nernst's Chain Mechanism. Nernst [47] explained the abnormal yield by introducing a different kind of chain reaction. He suggested that the primary action of light consisted in a dissociation of chlorine into atoms, these reacting by the sequence:

[47] *Z. Elektrochem.*, **24**, 335 (1918).

$$\begin{aligned} Cl + H_2 &\rightarrow HCl + H \\ H + Cl_2 &\rightarrow HCl + Cl, \text{ etc.} \end{aligned}$$

or by:

$$\begin{aligned} Cl + Cl &\rightarrow Cl_2 \\ H + H &\rightarrow H_2 \\ H + Cl &\rightarrow HCl. \end{aligned}$$

With the thermochemical data available at that time Nernst showed that the first two reactions were possible, a long chain of reactions being thus started by absorption of one quantum of light energy.

Göhring's Mechanism. Later, Göhring [48] showed that Nernst's mechanism could lead to a kinetic equation representing Bodenstein's experimental results. Assuming a sequence of reactions:

$$\begin{aligned} Cl_2 + h\nu &\rightarrow 2Cl && (k_1) \\ Cl + H_2 &\rightarrow HCl + H && (k_2) \\ H + Cl_2 &\rightarrow HCl + Cl && (k_5) \\ Cl + O_2 &\rightarrow ClO_2 && (k_9) \\ H + O_2 &\rightarrow HO_2 && (k_{11}) \\ \left(\begin{matrix} ClO_2 + Cl \rightarrow Cl_2 + O_2 \\ HO_2 + H \rightarrow H_2 + O_2 \end{matrix}\right) & \end{aligned}$$

he derived by the method, described in detail in connection with Bodenstein's theory, the following equation:

$$\frac{d[HCl]}{dt} = 2k_1 I_0 \frac{2k_2k_5[Cl_2]^2[H_2] + k_2k_9[Cl_2][H_2][O_2]}{[O_2](k_2k_{11}[H_2] + k_5k_9[Cl_2]) + k_9k_{11}[O_2]^2}$$

Neglecting the second term in the denominator on account of the low concentrations of oxygen and assuming $k_2 = k_5$; $k_9 < k_{11}$, this equation is brought to a form, in which it is in accord, not only with the experiments of Bodenstein and Dux, but also with the recent experiments of Thon.

Thon points out [49] that the identical formula is derived if, instead of free chlorine atoms, trichlorine molecules, Cl_3, be assumed as the reacting species. The sequence of reactions is then represented by the scheme:

$$\begin{aligned} &(1) \quad Cl_2 + h\nu \rightarrow 2Cl \\ &(2) \quad Cl + Cl_2 \rightarrow Cl_3 \\ &(3) \quad Cl_3 + H_2 \rightarrow 2HCl + Cl \\ &(4) \quad Cl + O_2 \rightarrow ClO_2 \\ &(5) \quad Cl_3 + O_2 \rightarrow ClO_2 + Cl_2 \end{aligned}$$

Thon suggests further that this second scheme is less objectionable than that used originally by Göhring.

The suggested atomic chain mechanisms seemed to be in disagreement with the observed non-reactivity of chlorine a very short time

[48] *Z. Elektrochem.*, 27, 511 (1921).
[49] *Loc. cit.*; see also *Fortschritte der Chem., Physik, physik. Chem.*, (A) 18, II (1926).

after illumination. Warburg,[50] for instance, calculated, on the basis of the original Nernst scheme, the mean life of chlorine atoms and came to the conclusion that, if these were formed, Bodenstein and Taylor should have observed a rapid rate of reaction on admixing chlorine to hydrogen. Göhring,[51] however, using his own reaction scheme, which includes the reaction of chlorine atoms with oxygen, calculated that in the experiments of Bodenstein and Taylor no measurable reaction could take place. Göhring's treatment is not sufficient for the explanation of Marshall's experiments, as, in these, oxygen-free chlorine was used. Marshall therefore suggests that chlorine atoms are "cleaned up" and recombine to the molecules on the walls of the narrow capillary connecting the illuminated chlorine with the hydrogen container.

Chapman's Theory. In extension of an earlier theory by Chapman and Whiston,[52] Chapman and Chapman [53] developed a theory giving a full account of Mrs. Chapman's experimental results, based on the assumption of active molecules. It was suggested that, in the illuminated gases, an equilibrium $Cl_2' + O_2 \rightleftarrows Cl_2 + O_2'$ is established, activated oxygen then occasionally combining with hydrogen to form water. The derived equation is:

$$\frac{d[HCl]}{dt} = \frac{k_1 [Cl_2]^2 [H_2]}{k_3 [H_2]^2 [O_2] + [Cl_2]}$$

and it is supposed also to account for the high quantum yield of the reaction, if the assumption be made, that the (active) hydrogen chloride molecules formed transmit their energy only to chlorine. Baly and Barker,[54] assuming a mechanism very similar to that of Bodenstein, suggest, however, that the transmission of the activation energy goes via re-emission and re-absorption of light, deducing from this assumption their observed lack of proportionality between the reaction rate and light intensity. This last deduction is erroneous and it can easily be shown that their theory leads to direct proportionality of light intensity and reaction.

Coehn's Mechanism. In order to explain the action of water vapour on the reaction rate, Coehn and Jung [55] suggest a reaction scheme of the Nernst type. The reaction in moist gases under the action of visible light is represented by the following scheme:

[50] *Z. Elektrochem.* **27**, 139 (1921).
[51] *Loc. cit.*
[52] *Loc. cit.*
[53] *J. Chem. Soc.*, **123**, 3079 (1923).
[54] *Ibid.*, **119**, 653 (1921).
[55] *Loc. cit.*

$$
\begin{array}{lll}
\text{I} & Cl_2 + h\nu \text{ (small)} & \rightarrow Cl_2' \\
 & Cl_2' + Cl_2 & \rightarrow Cl_2 + 2Cl \\
 & Cl + H_2O & \rightarrow HCl + OH \\
 & OH + H_2 & \rightarrow H_2O + H \\
 & H + Cl_2 & \rightarrow HCl + Cl \\
 & Cl + Cl & \rightarrow Cl_2, \text{ etc.}
\end{array}
$$

The dry gases in ultraviolet light are supposed to react by:

$$
\begin{array}{lll}
\text{II} & Cl_2 + h\nu \text{ (large)} & \rightarrow Cl_2'' \\
 & Cl_2'' + H_2 & \rightarrow Cl_2 + 2H \\
 & H + Cl_2 & \rightarrow HCl + Cl \\
 & Cl + Cl & \rightarrow Cl_2
\end{array}
$$

In support of their theory Coehn and Jung calculate that, thermodynamically, the direct reaction of a chlorine atom with a hydrogen molecule is rather improbable, if the recent thermochemical data on the heats of dissociation ($Cl_2 = 2Cl - 54{,}000$ cal.; $H_2 = 2H - 100{,}000$ cal.) be used. Further, the smallest energy quantum capable of causing the reaction chain II must be equal to the heat of dissociation of hydrogen and actually Coehn and Jung calculate from the wave length 3000 Å., 94,500 cal. as the lowest limit for it.

Norrish,[56] criticising the theory of Coehn, suggested that the reaction, in visible light, of moist gases was localised on the water film covering the walls of the reaction vessel. The recent results of Coehn and Heymer [57] indicate that this theory is not in accord with experiment, as it suggests a larger quantum yield of moist gases in ultraviolet light, but, actually, the identical value 10^4 was obtained. To support the reaction scheme II of Coehn's theory which excludes a chain reaction, Coehn and Heymer measured the quantum yield of *dry* gases in ultraviolet light and found, in good agreement with it, a value less than 7.

Weigert's Mechanism. Weigert [58] objects to Coehn's chain mechanism for the moist gases since it involves water molecules in the chain mechanism and therefore in the expression for the reaction velocity. The data of Bodenstein and Dux as to the absence of effect of water between wide limits contradict this. Weigert therefore suggests that water molecules are a component of the primary photochemical system, a cluster of hydrogen and chlorine molecules. The action of water is to facilitate an inner photoelectric effect between hydrogen and chlorine. His idea can be symbolised by the following scheme:

$$Cl_2 + h\nu + H_2 (+ H_2O) \rightarrow H_2^+ + Cl_2^- \text{ and}$$
$$H_2^+ + Cl_2^- \rightarrow HCl + H + Cl$$

[56] *J. Chem. Soc.*, 127, 2317 (1925).
[57] *Naturwiss.*, 14, 299 (1926).
[58] *Z. physik. Chem.*, 106, 426 (1923).

Cathala [59] makes a similar objection to Coehn's theory and develops a chain mechanism in which water does not take part in the chemical reactions but acts through its dipole nature, facilitating certain reactions of other components. The objection of Weigert to Coehn's theory is not fully justified. In fact the influence of water on the reaction velocity will be determined by the relative speeds of the reactions:

$$Cl + H_2O \rightarrow ClH + OH$$

and Nernst's $$Cl + Cl \rightarrow Cl_2, \text{ etc.}$$

Thus, it will be represented by an equation of the type

$$\frac{k_1 [H_2O] [Cl]}{k_2 [Cl]^2 + k_1 [H_2O] [Cl]}$$

which shows that, from a certain concentration upwards, the influence of water is negligible. Making use of a similar consideration, Cathala [60] calculated the rates of the two competitive reactions of chlorine atoms, concluding, as was mentioned before, that Coehn's mechanism cannot work. This calculation of Cathala is by no means conclusive since he arbitrarily assumes that the reaction of two chlorine atoms is successful on every collision. Coehn's theory, however, is not free from various other objections as, for instance, it does not explain the action of oxygen and, in its present form, leads to a reaction velocity equation in which the square root of the light intensity is involved. Chapman [61] suggests, therefore, that activated chlorine molecules are primarily formed and react with water to form a molecular compound which initiates a chain of reactions alternately with hydrogen and with chlorine molecules, hydrogen chloride being ultimately formed.

General Conclusions Concerning Mechanism. Comparing the two types of proposed chain reactions—those involving atoms and those with excited molecules—we note that, to reach a definitive decision at present is by no means easy. Undoubtedly, the recent measurements of Thon are more favourable to a reaction scheme of Göhring's type, but, when we consider how difficult it is to avoid all possible errors inherent in all kinetic measurements of a reaction which is so extraordinarily sensitive to traces of impurities, we must come to the conclusion that the experiments of Thon are not decisive. Besides, Thon assumes that the active mass of oxygen remains constant throughout

[59] *Compt. rend.*, **181**, 33 (1925).
[60] *Loc. cit.*
[61] *Proc. Farad. Soc.*, **21**, 547 (1925).

the course of reaction. If oxygen, as we shall see later, takes an active part in the reaction, water being formed, then the empirical equation of Thon should be modified and the agreement with Göhring's theory is partially lost. Other means of comparing the two rival theories on the reaction mechanism are by comparison with such experimental facts as: (1) the direct proportionality of the reaction rate and light intensity; (2) the rapid decrease of the quantum yield at very low pressures; (3) the influence of water vapour and, in connection with this, (4) the action of different wave lengths on dry and moist gases. The first point excludes all reaction schemes in which the recombination of the atoms to form initial molecules is assumed to be the cause of the limited length of a chain of reactions,[62] as all such theories unavoidably yield a final equation in which the square root of the light intensity is involved. Taking, for example, a simple case, we assume that the rate of reaction is *ceteris paribus* proportional to the concentration of chlorine atoms. The rate of their formation is in simple form:

$$+\frac{d\,[\mathrm{Cl}]}{dt} = k_1 I_0\,[\mathrm{Cl_2}];$$

the rate of disappearance:

$$-\frac{d\,[\mathrm{Cl}]}{dt} = k_2\,[\mathrm{Cl}]^2$$

from which equations it follows that the rate of reaction is proportional to

$$[\mathrm{Cl}] = \sqrt{\frac{k_1}{k_2} I_0\,[\mathrm{Cl_2}]}$$

By reason of this objection, however, all those atom chains are not excluded in which the rate of disappearance of reacting atoms is unimolecular with respect to their concentration, as, for instance, in the theory of Göhring. The decrease of the quantum yield at low pressures was found not only by Marshall in his paper already cited, but also by Marshall and Taylor,[63] who succeeded in realising one of the Nernst reactions by admitting atomic hydrogen to chlorine and bromine, but observed that the yield of hydrogen chloride per hydrogen atom increased rapidly at higher pressures. Taking account of this double evidence, the fact of a decreasing yield cannot be doubted. It would seem therefore that a mechanism in which activated molecules are involved, with their simultaneous deactivation by re-radiation (see

[62] See Berthoud, *Helv. chim. Acta*, 7, 324 (1923); Chapman, *Proc. Farad. Soc.*, 21, 547 (1925).

[63] *Nature*, 112, 937 (1923); see also Marshall, *J. Phys. Chem.*, 29, 842 (1925).

Bodenstein's theory, the reactions and constants 3 and 7), would give a more ready explanation of the facts. However, if we assume together with Marshall,[64] that chlorine atoms like those of hydrogen are "cleaned up" and recombine on the glass walls of the vessel, a decrease of the yield must be observed at low pressures. A careful investigation of the reaction rate at low pressures would probably give a definitive answer, for, the rate of deactivation of activated molecules is independent of the size of the vessel, whereas, if atoms take part in the reaction, the rate of clean up will be determined by the relation of their mean free path to the diameter of the vessel. A reaction mechanism based exclusively on the concept of activated molecules loses much of its plausibility when the action of water vapour is considered. The evidence of Jung's experiments, especially the different action of visible and ultraviolet light on dry gases strongly supports the view that chlorine atoms in the one case and probably hydrogen atoms in the other are the intermediate products of light action.

Spectral Evidence. From theoretical considerations on the relations between the absorption spectra and molecular binding of diatomic molecules,[65] Franck was led to the conclusion that halogen molecules can be dissociated on absorption of light, but, as was already discussed, one of the atoms formed should be in an excited "metastable" state.

The experimental study of the absorption spectra fully justified Franck's theory. Chlorine, as well as bromine and iodine, show, on closer investigation, a complicated system of absorption bands in the red and yellow part of the spectrum, converging to a limit, from which a continuous absorption extends towards the ultraviolet.[66] The convergence limit in Franck's interpretation represents the longest wave still capable of dissociating a halogen molecule into atoms, a normal and an excited one.

Recently, an exact spectroscopic determination of the energy levels of halogen atoms [67] has been undertaken. This determination permits one now to calculate exactly the amount of energy which is used for excitation of one of the atoms by light absorption, resulting in the dissociation of the halogen molecule. These values, which are very close to the earlier estimates of Franck, in combination with the quantum energy equivalent of the band convergence limit of the

[64] *Trans. Am. Elektrochem. Soc.*, 49, 143 (1926).
[65] See the first chapter.
[66] Mecke, *Ann. Physik*, 71, 104 (1924); Kuhn, *Z. Physik*, 39, 77 (1926).
[67] Turner, *Phys. Rev.*, 27, 397 (1926).

absorption spectra, yield values for the dissociation energy of halogens into two normal atoms which, being very close to the thermochemically determined values, once more confirm the theory of Franck. As an illustration, a table from Kuhn's [68] paper is reproduced here.

TABLE 16.

Halogen	Convergence limit (ν_c)	$Nh\nu_c$ in Cal.	Excitation energy of the atom $2P_2 - 2P_1$	Heat of dissociation	Heat of dissociation from thermochemical data
Cl_2	4785 Å.	59.4	2.5 Cal.	56.9 Cal.	57.0 Cal.
Br_2	5107	55.6	10.4	45.2	46.2
I_2	4995	56.8	21.6	35.2	34.5

In applying Franck's theory to the treatment of the hydrogen-chlorine reaction, we must bear in mind that Franck's arguments were developed for the case of an adiabatic dissociation of molecules absorbing light, i.e., a dissociation not induced by molecular collisions on light absorption. Another process is imaginable for molecules which absorbed energy quanta smaller than those of the convergence limit. If their mean life is of the usual order of magnitude, 10^{-7}—10^{-8} sec., then, at ordinary pressures, the activated chlorine molecules will suffer many collisions before emission of light and it is not certain that a molecule which has absorbed an energy quantum less than that of the convergence limit, but still comparable with the heat of dissociation into *two normal* atoms, cannot undergo this process by collision.

The question of the limiting wave length of the hydrogen-chlorine reaction has been the object of investigation, but so far no decisive results have been obtained. W. Taylor [69] claims that no reaction could be obtained with light of longer wave length than 4900 Å.—a value thus very close to the convergence limit. His results are, however, doubtful, as Coehn and Jung (*loc. cit.*) found a measurable reaction up to 5400 Å. (equivalent to 52,500 cal.). It is still uncertain whether this wave length actually represents the sensitivity limit, as the light absorption coefficient of chlorine in this spectral region becomes extraordinarily small, the amount of light energy absorbed being thus also very small. Certain it is from the experiments of Coehn and Jung that under the influence of red light, which is again more strongly absorbed, no reaction occurs. It will be seen from

[68] *Naturwiss.*, 14, 600 (1926).
[69] *Phil. Mag.*, 49, 1165 (1925).

this survey that, so far, none of the proposed theories can account for all the properties of the hydrogen-chlorine reaction.

The Fate of Oxygen in the Reaction. The theories of the hydrogen-chlorine reaction already discussed suggested that the active mass of oxygen remains constant to the end of the process.[70] However, Weigert,[71] as early as 1907, observed formation of water in a mixture of chlorine, hydrogen and oxygen illuminated by visible light.

Recently, Norrish and Rideal [72] studied the kinetics of the process. They found that the rate of formation of water could be expressed by the equation

$$\frac{d\,[H_2O]}{dt} = k\,[Cl_2]\,[O_2],$$

hydrogen concentration apparently not influencing the rate of reaction. This equation represents, however, only roughly, the experimental results. The velocity constants show a definite tendency to decrease when the ratio $\frac{H_2}{O_2}$ is being diminished, and particularly slow reaction is obtained with small absolute concentrations of oxygen and hydrogen.

The authors did not study the simultaneous formation of hydrogen chloride, considering it to be unimportant; but, from the data contained in their paper, one can estimate that the rate of formation of hydrogen chloride, even in these oxygen-rich mixtures, is about 5-10 times more rapid than the formation of water.

The theory of Norrish and Rideal implies the formation of activated chlorine molecules as the products of the primary action of light and the subsequent activation of oxygen on collisions with chlorine, this activated oxygen further reacting with hydrogen to form water. Introduction of other partial reactions (to account for the simultaneous formation of hydrogen chloride) leads the authors to a kinetic equation for the velocity of water formation, which is in agreement with the experimental data only when the reactions of activated chlorine with oxygen and hydrogen are negligibly slow in comparison with the rate of its spontaneous deactivation. Norrish and Rideal suggest, also, that the retarding effect of oxygen on hydrogen chloride formation has nothing in common with the observed formation of water, this being a primary reaction.

This proposed double action of oxygen seems to be an unnecessary complication. An estimation of the amount of water which could

[70] An exception is the theory of Chapman and Chapman, *loc. cit.*, where water formation is assumed.
[71] *Ann. Physik*, 24, 55, 243 (1907).
[72] *J. Chem. Soc.*, 127, 787 (1925).

be formed, for instance, in Bodenstein's experiments, shows that only a small portion of oxygen would be used up in this process, its active mass thus remaining approximately constant, as was assumed by Bodenstein. The question whether water formation is actually a primary reaction and not one induced by the chains forming hydrogen chloride cannot be answered at the present time. Tramm succeeded in preparing dry gases, which were not absolutely oxygen-free, but nevertheless did not react even on prolonged illumination by visible light. On the other hand, Chapman [73] relates that, in his laboratory, Hutton was unable to prepare dry oxygen-containing gases which were completely insensitive to visible radiation. This last result, further confirmed, will be a direct evidence that water formation is a primary photosensitised reaction, independent of hydrogen chloride formation, as was assumed by Norrish and Rideal.

The Phosgene Reaction. Another chlorine reaction, the formation of phosgene in visible light, shows much similarity to the photochemical formation of hydrogen chloride. Our knowledge of this reaction is, however, less advanced and, apparently, new kinetic measurements are required before an attempt to formulate a consistent theory of the process can be successfully undertaken.

Wildermann's [74] experiments with dry and purified mixtures of chlorine and carbon monoxide indicate that the rate of formation of phosgene can be expressed by the kinetic equation:

$$\frac{d\,[COCl_2]}{dt} = k\,I_0\,[Cl_2]\,[CO]$$

However, even with the utmost care with which the reacting gases were purified, the unknown and varying amount of oxygen still present diminishes the value of Wildermann's experiments. For, Chapman and Gee [75] showed that oxygen has a similar retarding effect on the rate of this reaction as on that of hydrogen and chlorine. The rate of phosgene formation is, however, inversely proportional to the oxygen concentration only when this latter is small, Chapman and Gee being able to represent their observations by the formula:

$$\text{Reaction velocity} = A + \frac{B}{[O_2]}$$

Chapman and Gee demonstrated also that the induction period observed in the reaction of chlorine with carbon monoxide by earlier investigators [76] is due, just as in the reaction of chlorine with hydro-

[73] *Trans. Farad. Soc.*, 21, 547 (1925).
[74] *Phil. Trans.*, 199A, 337 (1902); *Z. physik. Chem.*, 42, 257 (1903).
[75] *J. Chem. Soc.*, 99, 1726 (1911).
[76] Dyson and Harden, *J. Chem. Soc.*, 83, 201 (1903).

gen, to the presence of impurities, nitric oxide, ozone and nitrogen chloride being found very active in this respect.

The unusual observation was made by Chapman and Gee that, at higher temperatures (around 350°), the rate of photochemical reaction is manyfold slower than at room temperature. This effect was not very reproducible, but Chapman and Gee state that it was particularly marked when pure gases were used. With moist carbon monoxide, the decrease of the reaction velocity, though noticeable, was less pronounced.

The observations of Chapman and Gee were continued and considerably extended by Bodenstein and his co-workers,[77] who studied the kinetics of the reaction under varying conditions. The rate of formation of phosgene at room temperature with moist reactants is expressed, according to Bodenstein, fairly well by the equation:

$$+\frac{d\,[COCl_2]}{dt} = k\sqrt{I_{abs.}\,[CO]}\,.\,[Cl_2]$$

In this equation, however, is not included the retarding action of oxygen. Water, between the limits of 0.02 and 15 mm. vapour pressure, has very little influence on the rate of reaction. The temperature coefficient from 18° to 28° is equal to unity. Since, according to the above equation, the reaction velocity is proportional to the square root of the absorbed light energy, the quantum yield must be dependent on the intensity of the light source used. The determination of the quantum yield loses therefore much of its importance. Still, it is significant that, in the particular set-up of Bodenstein, as many as 1000 molecules of phosgene were formed per absorbed quantum. The reaction, therefore, must have a chain mechanism. We have seen previously that a very intensive drying suspended entirely the reaction between chlorine and hydrogen. The effect of a similar treatment on the rate of phosgene formation is not so far reaching. Still, the reaction proceeds some ten to one hundred-fold slower and now follows an entirely different equation:

$$+\frac{d\,[COCl_2]}{dt} = k\,I_{abs.}\,[Cl_2]\,.\,[CO]$$

The raising of the temperature by 200-300 degrees has a very similar effect on the reaction kinetics. Oxygen under these conditions loses almost entirely its retarding action.

Apparently, illuminated chlorine can, not only react with carbon monoxide with formation of phosgene, but can also induce the decom-

[77] *Rec. trav. chim. Pays Bas*, 41, 585 (1922); *Sitzb. Preuss. Akad.*, 13, 104 (1926).

position of this latter. This is indicated by the early observations of Weigert [78] that, at temperatures around 500°, the thermal equilibrium of phosgene and its decomposition products is not appreciably changed by illumination, although the rate of its attainment is considerably increased. We have already noticed a similar action of chlorine on sulfuryl chloride formation and decomposition.

Coehn and Becker [79] found that phosgene is decomposed at room temperature by ultraviolet light, a stationary state with about 4 per cent decomposition being reached in the total radiation of a mercury lamp. Bredig and Goldberg [80] noticed that, when mixtures of phosgene and hydrogen are illuminated by ultraviolet light, the decomposition of the former is almost complete and hydrogen chloride is formed.

Bodenstein [81] observed that the concentration of oxygen in an illuminated mixture of chlorine, carbon monoxide and oxygen does not remain constant, this latter reacting with carbon monoxide to form the dioxide. This reaction is photosensitised by chlorine as neither of the components absorbs visible light. In mixtures rich in oxygen, the rate of formation of carbon dioxide is even faster than that of phosgene. The kinetics of the reaction are complicated, as its full rate is attained only after some phosgene is formed, this latter playing some part in the reaction mechanism. The rate of carbon dioxide formation is directly proportional to the carbon monoxide concentration, less than directly proportional to that of chlorine and less than inversely proportional to the concentration of oxygen. It is probably not influenced by the presence of water vapour.

Altogether, the variety of kinetic relations observed in the reaction of chlorine and carbon monoxide is almost as large as in the reaction of chlorine and hydrogen. The observations on the rate of formation of phosgene are only incompletely linked together and therefore the postulation of some reaction mechanism accounting for all experimental data available would be somewhat premature. The study of the thermal formation and decomposition of phosgene led, on the other hand, to a complete explanation of the reaction mechanism. These reactions show less complications than the photochemical one; oxygen and traces of moisture, for instance, have no influence on their rate.

Christiansen,[82] and later Bodenstein and Plaut,[83] showed that the

[78] *Ann. Physik.*, **24**, 55 (1907).
[79] *Ber.*, **43**, 130 (1910).
[80] *Z. physik. Chem.*, **110**, 521 (1924).
[81] *Loc. cit.*
[82] *Z. physik. Chem.*, **103**, 99 (1923).

rates of formation and of decomposition of phosgene can be represented by the equation

$$+\frac{d\,[COCl_2]}{dt} = k\sqrt{[Cl_2]}\left(\frac{1}{k_1}[CO]\,[Cl_2] - [COCl_2]\right)$$

and derived this equation kinetically from the reaction scheme:

1. $Cl_2 \rightleftarrows 2Cl$ } thermal equilibria maintained
2. $Cl_2 + Cl \rightleftarrows Cl_3$ } during the reaction.
3. $Cl_3 + CO \rightleftarrows COCl_2 + Cl$ velocity determining processes.

Recently Bodenstein [84] attempted to explain the kinetics of the photochemical phosgene formation by means of a very similar set of intermediary processes:

1.	$Cl_2 + h\nu \rightarrow Cl_2'$	(k_1)
2.	$Cl_2' + CO \rightarrow CO' + Cl_2$	(k_2)
3.	$Cl_2' \rightarrow 2Cl$	(k_3)
4.	$Cl_2 + Cl \rightarrow Cl_3$	(k_4)
5.	$Cl_3 + CO \rightarrow COCl_2 + Cl$	(k_5)
6.	$Cl_3 \rightarrow Cl_2 + Cl$	(k_6)
7.	$Cl + Cl \rightarrow Cl_2$	(k_7)

From these, the equation can be deduced:

$$1.\quad +\frac{d\,[COCl_2]}{dt} = \frac{k_5 k_4\,[CO]\,[Cl_2]}{k_6 + k_5\,[CO]}\sqrt{\frac{k_1 \cdot k_3 \cdot I_{abs.}}{k_7\,(k_2[CO] + k_3)}}$$

which goes over into the equation obtained experimentally for moist gases at room temperature if the assumptions are made that:

$$k_6 >> k_5\,[CO]$$
$$k_2\,[CO] > k_3$$

$$2.\quad +\frac{d\,[COCl_2]}{dt} = \frac{k_5 k_4}{k_6}\sqrt{\frac{k_1 k_3 I_{abs.}}{k_7 k_2}}\,[CO] \cdot [Cl_2]$$

This equation, besides reproducing the observed relations of the reaction velocity to the concentrations of the reactants, enabled Bodenstein also to make a successful calculation of the absolute reaction velocity with only very few and quite relevant assumptions as to the velocity constants of the intermediary processes. This was possible since the processes 4, 5 and 6 occur also in the scheme proposed for the thermal reaction of chlorine and carbon monoxide; their velocity constants therefore are known from the measurements of the thermal reaction. $I_{abs.}k_1$ is the number of absorbed quanta which can be determined experimentally. There remains the ratio $\frac{k_3}{k_2}$ and the constant k_7. Bodenstein estimated the magnitude of the first one, using the observation that the kinetics of the photochemical reaction deviate

[84] *Loc. cit.*

slightly from the course prescribed by the simplified Equation 2 at small concentrations of carbon monoxide. With the values so determined, Bodenstein arrived at a number of phosgene molecules formed quite close to the measured value when he assumed that the reaction 7—the recombination of chlorine atoms to molecules—occurred on each or on a considerable fraction of all collisions (0.01—0.001) of the two atoms. This assumption is corroborated by the entirely independent observations on the rate of hydrogen bromide formation, to be discussed in the next section. It is obvious that Bodenstein's equation is a considerable step towards a complete elucidation of the reaction kinetics of the photochemical formation of phosgene. The retarding action of oxygen would not offer serious difficulties for a kinetic interpretation, since a reaction analogous to No. 2 of the above scheme would probably take account of it. The reaction kinetics with dry gases or at elevated temperatures remain unexplained by Bodenstein's mechanism. Under these conditions, suggests Bodenstein, no dissociation of the excited chlorine molecules into atoms takes place, the presence of dipole water molecules being necessary for this process. In how far this conception is in agreement with information otherwise obtained will be seen from a later discussion. At present, it should be pointed out that the reaction mechanism in the form postulated now by Bodenstein for moist gases must necessarily remain somewhat doubtful so long as Bodenstein's view on the action of water vapour has not been confirmed.

The Hydrogen-Bromine Combination

In our discussion of the hydrogen-chlorine reaction, we devoted little attention to the reactions occurring under the action of alpha particles and x-rays and to the thermal reaction. This was admissible, since the study of these reactions, yielding, in general, similar results with respect to the complexity of the kinetic relations,[85] did not contribute appreciably to our knowledge of the mechanism of the photochemical reaction.

With the study of an analogous reaction of bromine—the photochemical formation of hydrogen bromide—the opposite condition of affairs is found. In this case, knowledge of the kinetic mechanism of the thermal reaction enabled Bodenstein to predict the kinetics of the photochemical process. The experimental study led, in his hands, to a most brilliant success for the modern treatment of gaseous ki-

[85] Bodenstein, *Z. Elektrochem.*, 22, 53 (1916).

netics, yielding a complete agreement with the theory. Also, certain results were obtained which are of importance for the general theory of chemical reactions in the gaseous phase. The sensitivity to light of a mixture of bromine and hydrogen was first noticed by Kastle and Beatty,[86] who observed hydrogen bromide formation in sunlight at temperatures between 100° and 200°, a rapid increase of reaction velocity with temperature being reported. Coehn and Stuckard[87] observed, as we have already noted, a quantitative formation of hydrogen bromide at 270° in the light absorbed by bromine. Pusch[88] estimated the quantum yield of this reaction at room temperature, arriving at a value less than 0.001 molecules per quantum. Nernst gave an explanation of this low yield from the standpoint of the primary formation of bromine atoms, calculating the thermodynamic "impossibility" of the reaction $Br + H_2 \longrightarrow HBr + H$.

Later, Bodenstein and Lütkemeyer[89] studied the reaction kinetics quantitatively at 160° to 218°. The progress of the reaction was followed photometrically, the total radiation of a "Pointolite" lamp being used for the experiments. The absorbed light energy was measured with the gases cooled to room temperature. A possible error connected with a change in the absorption with varying temperatures was eliminated by Bodenstein and Lütkemeyer, who showed spectrophotometrically that only in the longer wave length region is the absorption of light by bromine appreciably increased. In the shorter and more strongly absorbed region, the amount absorbed was hardly affected by a temperature change of 200°.

The rate of reaction, studied with and without an initial addition of hydrogen bromide, was in good accord with the following equation the meaning of which will be interpreted in the subsequent pages.

$$\frac{d\,[HBr]}{dt} = k\sqrt{I_{abs.}}\,\frac{[H_2]}{1 + \dfrac{[HBr]}{10[Br_2]}}$$

According to this equation, the rate of reaction is proportional to the square root of the absorbed light energy and is retarded by hydrogen bromide, besides being proportional to the hydrogen concentration. The measurements of the temperature coefficient in the temperature range, 160-218°, yielded a very large value, about 1.5 for a 10° temperature increase. In order to understand the kinetic mechanism underlying the equation given, we have first to discuss the kinetics

[86] *J. Am. Chem. Soc.*, **20**, 159 (1898).
[87] *Loc. cit.*
[88] *Z. Electrochem.*, **24**, 336 (1918).
[89] *Z. physik. Chem.*, **121**, 127 (1926).

of the thermal formation of hydrogen bromide, this reaction being the object of an investigation by Bodenstein and Lind.[90] The thermal reaction was studied in the temperature range 228-302°, the authors representing their kinetic measurements by the empirical formula:

$$+\frac{d\,[2HBr]}{dt} = \frac{k\,[H_2]\,\sqrt{[Br_2]}}{5 + \dfrac{2[HBr]}{[Br_2]}}$$

or, if reduced to [1 HBr] unit:

$$\frac{d\,[HBr]}{dt} = 2/5\; k_{Lind}\,\frac{[H_2]\,\sqrt{[Br_2]}}{1 + \dfrac{[HBr]}{10[Br_2]}}$$

In attempting to explain this equation kinetically, Bodenstein and Lind suggested that the square root indicated that bromine atoms and not bromine molecules reacted with hydrogen to form hydrogen bromide.

The full theory of this reaction was given independently by Christiansen,[91] Herzfeld,[92] and Polanyi,[93] these authors suggesting that the following sequence of reactions takes place:

(1)	$Br_2 \rightarrow 2Br$	(k_1)
(2)	$Br + H_2 \rightarrow HBr + H$	(k_2)
(3)	$H + Br_2 \rightarrow HBr + Br$	(k_3)
(4)	$H + HBr \rightarrow H_2 + Br$	(k_4)
(6)	$Br + Br \rightarrow Br_2$	(k_6)

The kinetic interpretation of these equations and the assumption that, in the steady state, the concentrations of bromine and hydrogen atoms are constant led to the final expression for the rate of reaction, which is identical with the empirical equation of Bodenstein and Lind:

$$\frac{d\,[HBr]}{dt} = \frac{2\,k_2\,[H_2]\,\sqrt{\dfrac{k_1}{k_6}\,[Br_2]}}{1 + \dfrac{k_4}{k_3}\,\dfrac{[HBr]}{[Br_2]}}$$

A very interesting property of the suggested mechanism is that the concentration of the bromine atoms is unchanged by the formation of hydrogen bromide by reactions 3 and 4, being solely determined by reactions 1 and 2, and being thus calculable from the thermal dissociation constant of bromine vapour.

Herzfeld estimated the probable relative velocities of the reactions 2, 3, and 4, and suggested that the last two, being exothermic, occurred on almost every collision of the hydrogen atoms with molecules of

[90] *Z. physik. Chem.*, 57, 168 (1907).
[91] *Danske Vid. Math. Phys. Medd.*, 1, 14 (1919).
[92] *Z. Elektrochem.*, 25, 301 (1919); *Ann. Physik*, 59, 635 (1919).
[93] *Z. Elektrochem.*, 26, 50 (1920).

bromine and hydrogen bromide. "Almost every" collision was necessary because Bodenstein and Lind found the ratio $\frac{k_4}{k_3}$ to be equal not to unity but to 0.1 and the only slightly different molecular radii of hydrogen and hydrogen bromide could not account for this factor. Herzfeld therefore suggested that the reaction $H + HBr \longrightarrow H_2 + Br$ occurred only with a certain orientation of the components at the moment of collision, calling this condition a "steric factor." The reaction of the bromine atom and hydrogen molecule is endothermic and probably requires a certain amount of activation energy for its success, being thus much slower than the reactions 3 and 4. The steady concentration of bromine atoms must be therefore much larger than the concentration of hydrogen atoms, which justifies the omission of: 5. $H + H \rightarrow H_2$ in the general scheme of reactions occurring. We can calculate the activation energy of reaction 2 by two different methods.[94] First, by knowing the bromine atom concentration from the dissociation constant of the bromine vapour,[95] the total number of collisions between bromine atoms and hydrogen molecules is calculated (I) and is compared with the number of "successful" collisions (II) (for instance, when the hydrogen bromide concentration is very small, two hydrogen bromide molecules are formed for each bromine atom reacting). The ratio $\frac{(II)}{(I)}$ is equated to $e^{-\frac{q_2}{RT}}$, q_2 being the activation energy of the reaction 2. The other method is based on the kinetic interpretation of the Arrhenius equation $\frac{d\,ln\,k}{dT} = + \frac{q}{RT^2}$. The temperature coefficient of the thermal reaction of bromine with hydrogen as determined by Lind is, however, dependent not only on the temperature coefficient of the reaction 2 but also on the change in bromine atom concentration with temperature. We have then:

$$2/5\, k_{Lind} = 2k_2 \sqrt{\frac{k_1}{k_3}} \text{ or } \frac{k_{Lind}}{5} = k_2 \sqrt{K_{Br_2}}$$

(K_{Br_2} being the dissociation constant of bromine vapour)

and

$$\frac{d\,ln\,k_{Lind}}{dT} = \tfrac{1}{2} \frac{d\,ln\,K_{Br_2}}{dT} + \frac{d\,ln\,k_2}{dT}$$

From this equation $\frac{d\,ln\,k_2}{dT}$, and therefore q_2, can be calculated, since both other terms are known.

[94] Comp. Jeans, "Dynamical Theory of Gases," or Hinshelwood, "Kinetics of chemical change in gaseous systems." Oxford, 1926.
[95] Bodenstein and Cramer, *Z. Elektrochem.*, 22, 327 (1916).

These two methods of calculation yield for q_2 an almost identical value of about 17,000 cal. We will not enter into further discussion of the very interesting application of this value to the calculation of the heat of dissociation of hydrogen molecule, made by Herzfeld,[96] and later by Bodenstein and Jung,[97] but will return to the discussion of the kinetics of the photochemical reaction. Bodenstein suggested that the primary action of light consisted in the dissociation of a bromine molecule into atoms, two atoms being thus formed for each absorbed quantum. The subsequent reactions were supposed to be identical with those of the thermal reaction. Putting the number of absorbed quanta per second equal to a and calculating the rate of reaction in the usual manner we arrive at the equation identical with that given on page 105:

$$+\frac{d\,[\mathrm{HBr}]}{dt}=\frac{2\,k_2\,[\mathrm{H_2}]\,\sqrt{\frac{a}{k_6}}}{1+\frac{k_4}{k_3}\,\frac{[\mathrm{HBr}]}{[\mathrm{Br_2}]}}$$

Inasmuch as a is independent of temperature and k_6 (the rate of formation of bromine molecules from the atoms) is of the order of the molecular collisions number and thus dependent only on $\sqrt{T_{\mathrm{abs}}}$, the temperature coefficient of the photochemical reaction is determined by k_2. Therefore, if the suggested mechanism is correct, it must be possible to calculate this temperature coefficient by means of the activation energy q_2 as obtained from the thermal reaction measurements. The following table shows the degree of agreement of measured and calculated values.

TABLE 17.

$T_{\mathrm{abs.}}$	$\log k_{\mathrm{calc.}}$*	$\log k_{\mathrm{meas.}}$	diff.
491	−2.630	−2.690	+0.060
467	−3.035	−2.983	−0.052
456	−3.232	−3.190	−0.042
447	−3.405	−3.425	+0.020
433	−3.684	−3.699	+0.015

* $k=2k_2\sqrt{\frac{a}{k_6}}$

Bodenstein rightly points out that this very good agreement is the strongest argument in favour of the whole reaction mechanism proposed. A calculation of the quantum yield is naturally meaningless for this reaction, but the knowledge of the number of absorbed quanta

[96] *Loc. cit.*
[97] *Z. physik. Chem.*, 121, 127 (1926).

enabled Bodenstein to estimate the rate of combination of bromine atoms to molecules. This calculation, being of far-reaching importance for the theory of gaseous reactions in general, will now be discussed.

From the calculated kinetic equations, it will be seen that the rate of photochemical, as well as thermal, reaction is proportional to the stationary concentration of bromine atoms and therefore

$$[\mathrm{Br}]_{\text{light}} = [\mathrm{Br}]_{\text{dark}} \times \frac{\text{light velocity}}{\text{dark velocity}}$$

The concentration of the bromine atoms in the dark and the velocity of the thermal reaction at 218° can be calculated from the combined extrapolated measurements of Cramer (*loc. cit*) and of Lind (*loc. cit*). The results show that the concentration of bromine atoms in light is about 300 times larger than in the dark. The number of bromine atoms formed per second is equal to twice the number of absorbed quanta. Since white light was used in the experiments of Bodenstein and Lütkemeyer they calculated this number for a mean wave length of 4300 Å. In the stationary state, the number of bromine atoms recombining to molecules must be equal to the number formed, thus to 2a. Comparing this number of "successful" collisions with the total number of collisions of two bromine atoms, calculated for their concentration in light and using an assumed atom diameter of 3×10^{-8} cm., Bodenstein found that only about 0.0013 of all collisions led to the formation of molecules, this fraction showing only irregular variations for different pressures and temperatures. The very low yield of this reaction is in general agreement with the more recent theoretical considerations of Polanyi,[98a] Herzfeld [98b] and Christiansen,[98c] as well as with those of Born and Franck,[98d] that the "quasi-molecules," formed on collision of two atoms, possess a large excess of energy in some intramolecular form and must therefore either get rid of it within a short time [99] by collision with some neutral molecule or fall apart again. The calculations of Bodenstein confirm the small influence of temperature on the yield of the atomic reaction, predicted by these theories, but are in conflict with them, inasmuch as Bodenstein does not find the pronounced influence of the total pressure which should follow from the assumed rôle of neutral molecules. Bodenstein

[98a] *Z. Physik*, 1, 337 (1920).
[98b] *Ibid.*, 8, 132 (1922).
[98c] *Z. physik Chem.*, 103, 91 (1923).
[98d] *Z. physik*, 31, 411 (1925); *Ann. Physik*, 76, 225 (1925).
[99] In the opinion of Franck and Born this is the time required for the quantisation of the newly formed non-quantized molecules and is of much shorter duration than the usually observed mean life of activated molecules (10^{-7}—10^{-8} sec).

admits, however, that his measurements are not exact enough for a final decision.

The reaction between bromine and hydrogen is of interest from still another point of view. In the studies of kinetics of those photochemical reactions which are accompanied by a thermal process of measurable velocity, the assumption has almost generally been tacitly made that each of the reactions, although taking place simultaneously with the other, does not influence its rate. Consequently, the rate of photochemical reaction is usually determined by subtracting from the total rate observed on illuminaion the (calculated or measured) rate of thermal reaction. In the opinion of Plotnikoff [100] the assumption hereby made is generally valid and is called by him the additivity law. It can, however, be easily demonstrated that this so-called law fails completely [101] in the case of bromine and hydrogen. Indeed, if thermal and photochemical reaction rates are simply added, then the total rate on illumination is represented by the equation:

$$+\frac{d[\mathrm{HBr}]}{dt} = k\frac{[\mathrm{H_2}]\left(\sqrt{k_1[\mathrm{Br_2}]} + \sqrt{I_{\mathrm{abs.}}}\right)}{1 + \frac{[\mathrm{HBr}]}{10[\mathrm{Br_2}]}}$$

whereas the correct equation, derived on the basis of the experimentally confirmed reaction mechanism, is: [102]

$$+\frac{d[\mathrm{HBr}]}{dt} = k\frac{[\mathrm{H_2}]\sqrt{I_{\mathrm{abs.}} + k[\mathrm{Br_2}]}}{1 + \frac{[\mathrm{HBr}]}{10[\mathrm{Br_2}]}}$$

The non-equality of both expressions is obvious. So far, only in this one case, has the failure of the additivity rule been established and undoubtedly there is no reason to suggest that reactions with simpler kinetic relations do not follow the rule of Plotnikoff. In cases, however, where fractional exponents of the light intensity and of reactant concentrations enter into reaction velocity equations, it can only be decided by special experiments or by demonstration, that values for the photochemical reaction rate, calculated in the usual way, yield a simple law which can be interpreted in terms of a definite reaction mechanism.[103]

The Reaction of Halogens with Potassium Oxalate

The Iodine Reaction. Atomic reaction chains, the introduction of which led gradually to a complete kinetic interpretation of the

[100] Comp. "Lehrbuch."
[101] Comp. Berthoud, *J. chim. phys.*, 23, 251 (1926).
[102] In the experiments of Bodenstein and Lütkemeyer the temperature was chosen so low, that the correction relating to the thermal reaction was negligible as compared with other experimental errors.
[103] Kistiakowsky, *Z. physik. Chem.*, 117, 337 (1926).

hydrogen-bromine reaction, as has been shown on previous pages, proved also to be very useful in the discussion of the reactions of iodine and bromine with potassium oxalate. These reactions have been studied in aqueous solutions at room temperature, but, nevertheless, in respect to the kinetic mechanism, they both are strikingly similar to the gaseous reaction already discussed.

The reduction of iodine by potassium oxalate was studied by Dhar,[104] who obtained rather contradictory results. In the dark, the reaction is of the first order with respect to iodine and has a very high temperature coefficient. The reaction is accelerated by light and Dhar suggests that there is an optimum spectral region situated in the "indigo" region of the visible spectrum. The temperature coefficient of the light reaction is much lower than that of the dark one, but is still very high, Dhar giving, in one paper, the value 3.4, in the other, 2.68. The photochemical reaction was determined by Dhar, first as unimolecular with respect to iodine, later as proportional to $[I_2]^{1/2}$. In his last paper, Dhar gives a calculation of the quantum yield, finding a much lower value than corresponding to the equivalence law. Berthoud and Bellenot[105] obtained very interesting results by studying the kinetics of the dark and light reaction. In the dark, the rate of reaction was found to be, in agreement with Dhar's results, unimolecular with respect to iodine and potassium oxalate and inversely proportional to the potassium iodide concentration, this latter being present in excess of iodine. The action of iodide ion was interpreted in this way: the free iodine molecules were suggested as the reacting component, and not the tri-iodide ions. The concentration of the free molecules is determined by the equilibrium $\frac{[I_2][I^-]}{[I_3^-]} = K$ from which the retarding action of the iodide ion can be easily deduced. The temperature coefficient of the dark reaction was found to be 4.86 (for 10°) between 66° and 78°.

The study of the spectral sensitivity of the reaction, an incandescent lamp and different light filters being used, revealed that all visible rays from 7000 to 4100 Å. are active in increasing the rate of reaction. An approximate calculation of the relative amounts of light energy absorbed by iodine indicated rather that no pronounced maximum of activity of a certain spectral region exists, although the red rays were only slightly, and blue and violet completely, absorbed

[104] *Proc. K. Akad. Wetens. Amsterd.*, 16, 1097 (1916); *Ann. de Chim.*, 11, 130 (1919); *J. Chem. Soc.*, 123, 1856 (1923); *Z. Elektrochem.*, 31, 621 (1925).
[105] *Helv. chim. Acta*, 7, 307 (1923); *J. chim. phys.*, 21, 308 (1924).

by iodine in the concentrations studied. The subsequent separate study of the reaction in red and in blue light showed that the rate was proportional to the potassium oxalate and inversely proportional to the potassium iodide concentrations, independent of the kind of light used. With respect to these two reaction components we thus have relations identical with those of the dark reaction. It must be noted that in the experiments of Berthoud and Bellenot a large excess of these substances relative to iodine was always present. Assuming the rate of reaction to be proportional to the absorbed light energy we would expect to find in red light a unimolecular reaction with respect to iodine and in blue light a reaction of zero order. However, the constants calculated by means of the corresponding equations show a marked tendency to increase in red, as well as in blue light. A very good constancy was obtained in the whole course of reaction and for different initial concentrations of iodine if the constants were calculated on the assumption that, in red light, the reaction velocity is proportional to the square root of the iodine concentration and, in blue light, inversely proportional to its square root. These kinetic relations indicated that the rate of reaction might be proportional also to the square root of the light intensity. Actual measurements, for which a rotating disc with varying numbers of open sectors was employed, fully justified this expectation; in red as well as in blue light doubling the intensity increased the rate by the factor (mean) 1.43; the factor (mean) 2.00 being obtained when the intensity was increased fourfold. These relations held, however, only when the speed of rotation of the disc was high. When the time of interruption increased, different relations were found, the reaction velocity tending, for a very long interruption, to become proportional to the time of illumination. Table 18 shows the results of Berthoud and Bellenot.

TABLE 18.

Time of illumination	Duration of an interruption in seconds	$\frac{\Delta x}{\Delta t}$
Light 4/4	0.000	0.208
	0.022	0.104
	0.080	0.103
	0.166	0.098
	0.197	0.091
Light 1/4	0.300	0.082
Dark 3/4	1.83	0.071
	15.	0.066
	75.	0.062
	180.	0.060
	450.	0.060

The temperature coefficient of the light reaction in the temperature interval 25°-40° was found to be 3.22 in red and 3.15 in blue light.

Berthoud and Bellenot, discussing the relations described, came to the conclusion that all the observed kinetic relations can be explained by assuming that the primary action of light consists in the dissociation of an iodine molecule into atoms. However, only the free iodine molecules and not the ions I_3' are supposed to react in this way on absorption of light. Berthoud and Bellenot further suggest that the iodine atoms either recombine to form molecules or react by

$$\text{(a)} \quad C_2O_4K_2 + I \rightarrow C_2O_4K + I^- + K^\cdot$$

which reaction is slow and is followed by a rapid reaction

$$\text{(b)} \quad C_2O_4K + I_2 \rightarrow 2CO_2 + I + I^- + K^\cdot$$

The authors consider also the possibility of the following reactions:

$$\text{(a')} \quad C_2O_4^{--} + I \rightarrow C_2O_4^- + I^-, \quad \text{(b')} \quad C_2O_4^- + I_2 \rightarrow 2CO_2 + I + I^-.$$

The result of these two subsequent reactions is that the steady concentration of iodine atoms in an illuminated solution is not materially affected by their reaction with oxalate ion. The kinetic interpretation of the suggested reactions leads, however, to an equation which is inconsistent with the experimental results. In order to obtain an equation which is capable of representing all the experimental data, Berthoud and Bellenot assume that the recombination of iodine atoms to molecules can occur only if an iodide ion is present, the tri-iodide ion being thus formed. For the experiments in light only slightly absorbed by iodine (red) we have then the following set of equations:

$$\text{(1)} \quad +\frac{d[I]}{dt} = I_0 k_1 [I_2]$$

$$\text{(2)} \quad -\frac{d[I]}{dt} = k_2 [I]^2 [I^-]$$

$$\text{(3)} \quad -\frac{d[C_2O_4]}{dt} = k_3 [C_2O_4K_2] [I]$$

$$\text{(4)} \quad \frac{[I_2][I^-]}{[I_3^-]} = K$$

from which the final equation

$$\text{(5)} \quad -\frac{d[C_2O_4K_2]}{dt} = k_3 \sqrt{\frac{I_0 k_1 K}{k_2} [I_3^-]} \frac{[C_2O_4K_2]}{[I^-]}$$

is easily deduced. Inasmuch as the constant K of Equation 4 is small and the bulk of iodine is therefore present in the solution as I_3^-, this equation fully accounts for the experimental data obtained in red light.

We will not reproduce in detail the mathematical derivation of

the equation for the case of very strongly absorbed blue light, limiting ourselves to the following remarks.

The blue light is strongly absorbed not only by the iodine molecule, but also by the ion I_3^-. Therefore, the part which is absorbed by the former will be dependent on the concentrations of both light absorbing components, being determined (see page 39) by the equation

$$\frac{I_{\text{abs. } T_2}}{I_{\text{abs. total}}} = \frac{\alpha_1 [I_2]}{\alpha_1[I_2] + \alpha_2[I_3^-]}$$

or, neglecting $\alpha_1 [I_2]$ in the denominator, by

$$\frac{I_{\text{abs. } T_2}}{I_{\text{abs. tot.}}} = \frac{\alpha_1 [I_2]}{\alpha_2 [I_3^-]}.$$

This expression, being introduced into the general scheme of reactions instead of Equation 1 of the preceding page, yields a final expression in which the iodine concentration enters as the zero power. Experimentally, the inverse proportionality to the square root of the iodine concentration was found. To arrive at a better agreement we must assume—keeping in mind, that almost all the light is absorbed already by the first layers of the solution—that no diffusion of iodine atoms takes place, the reaction being limited to the illuminated space. Then, in a layer of the thickness dx, an amount of light $I_x \alpha_1 [I_2] dx$ will be absorbed by the iodine molecule, each layer having its own steady concentration of the iodine atoms. If, now, the concentration of iodine be increased n-fold, then the concentration of the iodine atoms will be increased (comp. page 96) by the factor $\sqrt{n}$, but the thickness of the layer in which the same amount of light energy is absorbed will be decreased by the factor n. Thus, the integral reaction velocity, which is equal to the integral of the local velocity over the illuminated space, will be decreased by the factor $\sqrt{\frac{1}{n}}$. A more exact mathematical calculation based on the reaction mechanism suggested on p. 113, but taking into account the changed conditions of light absorption, leads to the final equation:

$$-\frac{d[C_2O_4K_2]}{dt} = k \sqrt{\frac{I_0}{[I_3^-]}} \frac{[C_2O_4K_2]}{[I^-]}$$

which is in agreement with the experimental data. Berthoud and Bellenot demonstrated also that when stirring of the solution was used, the retarding action of iodine diminished, the "order" of reaction with respect to this component being closer to zero, these experiments thus indicating the correctness of the assumption that diffusion of

iodine atoms is negligible in unstirred solutions. We have already noted that Berthoud and Bellenot studied the influence of the incident light intensity by means of a rotating disc with open sectors placed between the light source and the reaction vessel. The fact that they obtained a square root proportionality, implies that the photochemical reaction proceeds a measurable time after each illumination, a certain steady concentration of the iodine atoms being maintained by the intermittent light. It is obvious that, if the reaction ceases immeasurably fast after each illumination, no matter what the real relation may be, a direct proportionality to the "mean intensity" will be found if use of some sort of intermittent light be made for the experiments. Further evidence concerning the chain mechanism is furnished by Table 18 on page 112, which indicates that the time for the completion of a chain is by no means immeasurably fast, being of the order of a second. The steady concentration of the iodine atoms in the illuminated solution must therefore be relatively very high and in apparent disagreement with this fact, is the comparatively low yield of the reaction, Berthoud and Bellenot calculating that, for each quantum of light absorbed by the iodine molecule I_2, about 3 oxalate molecules are oxidised. The disagreement is only apparent, as the high temperature coefficient of the photochemical reaction indicates that the reaction

$$C_2O_4K_2 + I \rightarrow C_2O_4K + I^- + K^\cdot$$

requires a large activation energy, equal to about 19,000 cal., so that only very few of the collisions can be successful. It seems to be more difficult to explain why the iodine atoms do not recombine to molecules, as an approximate calculation shows that, during the "life" of an iodine atom, it suffers many collisions with other atoms. Berthoud and Bellenot assume that the recombination goes only via tri-iodide ion, for which reaction a collision of three bodies is necessary. This is in agreement with the kinetic results and explains to a certain extent the slowness of the recombination. However, the explanation is very formal and the reason why the iodine atoms do not recombine directly to the molecules is left unknown, since, in a solution, there are enough collisions with the solvent molecules to take away all excess energy, a process which is necessary for the success of atomic recombination, according to the theories of Polanyi and others already given. The experiments of Berthoud and Bellenot strongly support the view that, in solution at least, iodine is dissociated into atoms by light of far longer wave length than that of the convergence limit of the absorption

bands in gaseous iodine. The efficiency of light of different wavelengths in producing the dissociation was only estimated by the authors, who suggest that probably no difference exists between the action of the red and yellow regions. We have already discussed on page 64 the reaction of iodine with ferrous ions. We had the same light-absorbing component and the same reaction, reduction of iodine, but the kinetics of both processes are extraordinarily different. The quantum yield in the former reaction was found to be unity and the reaction is proportional to the light intensity, as the same yield was obtained by Rideal and Williams and by Kistiakowsky although the light intensity in both these determinations was considerably different. Another important difference is that the reaction with iron salts is independent of the concentrations of the reacting species. Less importance should be ascribed to the inefficiency of red rays observed by Rideal and Williams, as, apparently, the spectral sensitivity measurements of these authors were not very accurate.

A certain indication as to the real cause of the observed differences can be deduced from the temperature coefficients of both photochemical reactions. We have seen that one is strongly accelerated by temperature increase, whereas the other, according to Rideal and Williams, is practically independent of temperature. This last fact may mean that the reaction of the primary product of light action with ferrous ion is one not requiring a large activation energy and therefore very fast, faster at least than the rate of deactivation.

Kistiakowsky [106] has suggested two possible reaction mechanisms for the iodine-ferrous ion reaction. Inasmuch as in this reaction not only the iodine molecules, but also the tri-iodide ions, are effective, while Berthoud and Bellenot demonstrate that only the former are dissociated into atoms, we must assume that not only iodine atoms, but also the activated tri-iodide ions are capable of reaction with ferrous ion. This of course implies that the reaction scheme of Berthoud and Bellenot is correct. We see also, why no chains are formed in the iodine-ferrous ion reaction. Here we have

$$Fe^{\cdot\cdot} + I \rightarrow Fe^{\cdot\cdot\cdot} + I^-$$

or

$$2Fe^{\cdot\cdot} + I_2^- \rightarrow 2Fe^{\cdot\cdot\cdot} + 3I^-$$

whereas the similar reaction with the divalent oxalate ion must cause the formation of a new iodine atom, thus starting a chain.

The Reaction of Bromine. The action of bromine on potassium oxalate, also studied by Berthoud and Bellenot,[107] shows very great

[106] *Loc. cit.*, page 65.

[107] *Loc. cit.* Roloff, *Z. physik. Chem.*, 13, 364 (1894), has studied the action of bromine on oxalic acid, directing his attention mostly to the thermal reaction. His

similarity to the reaction of iodine. We will therefore mentio the points of difference.

The study of the spectral sensitivity indicates that only ligh shorter wave length than approximately 5400 Å. is effective. Th kinetic measurements, carried out with the total radiation of an incandescent lamp, indicate that the retarding action of bromide ion on the rate of photochemical reaction is negligible, whereas the thermal reaction follows the equation found for iodine. The rate of reaction, if the concentration of bromine is small (0.005 n) and the light absorption therefore but slight, is proportional to the square root of the bromine concentration. In more concentrated solutions of bromine the reaction velocity is independent of its concentration. The experiments with intermittent light, yielding the same relations as for iodine, indicate that the mechanism of the bromine reaction is in essentials similar to that of iodine.

Berthoud and Bellenot, pointing out the observed differences in the behaviour of both reactions, suggest that light is capable of dissociating not only the bromine molecules but also the tri-bromide ion Br_3^-. This suggestion is in agreement with observations of Roloff [108] and explains the absence of the retardation by bromide ion, if the further assumption be made, that bromine atoms recombine directly to the molecules and not to the ions Br_3^-. As to the zero order of reaction with complete absorption of light, Berthoud and Bellenot remark that light absorption by bromine of the concentrations studied is much weaker than by iodine, so that a measurable if not uniform absorption of light takes place in the whole mass of the solution. The consideration, leading to the inverse proportionality with the square root of the light-absorbing component is, therefore, not applicable to the bromine reaction, unless much more concentrated solutions be used. For these, if the theory is correct, similar relations to those for iodine should be found.

These two chain reactions in solution belong to the very few examples of photochemical reactions in liquid phase for which a complete explanation of the kinetics has been nearly achieved so far. There are enough indications, however, to suggest that a numerous group of photochemical reactions—the halogenations of organic compounds—have also some kind of chain mechanism, though their kinetics have been the object of only an incomplete study.

experiments on the rate of photochemical reaction indicate that this is more complicated than the reaction in neutral solution studied by Berthoud and Bellenot.

[108] *Loc. cit.*

The Halogenation of Carbon Compounds

Chlorination of Benzene. A well known reaction is the action of chlorine on benzene, hexachlorobenzene being formed. Slator,[109] studying this reaction in light, observed the proportionality of the reaction rate to the square of the chlorine concentration.

Luther and Goldberg [110] demonstrated that Slator's results were due to a varying amount of oxygen dissolved in benzene, the reaction velocity being apparently proportional to the chlorine concentration. Oxygen shows a strong inhibitive effect on the reaction velocity. Its active mass, however, apparently does not remain constant through the course of reaction, the velocity curves showing a typical auto-catalytic S shape. Luther and Goldberg suggest that, in the course of the reaction, the oxygen present is used up in some way and support their view by the observation that, the larger the chlorine concentration and therefore the initial velocity, the sooner the auto-catalytic increase of the reaction velocity begins. The inhibitive effect of oxygen is very pronounced; for instance, the reaction velocity in benzene which has been degassed by evacuation is about 75 times faster than in benzene saturated with oxygen of 3.5 atmospheres pressure.

Bodenstein [111] estimated the yield of chlorination of oxygen-free benzene to be as high as 10^6 molecules per quantum of absorbed light.

Chlorination of Toluene. Luther and Goldberg [112] demonstrated also that the photochemical chlorination of toluene, xylene, and acetic acid were sensitive to oxygen, the retarding effect of this latter being apparently not so pronounced as in the case of benzene. Book and Eggert [113] observed that chlorine reacted with toluene in light even at −80°, the rate of the thermal reaction being negligible at this temperature. The chlorination took place in the side chain, about 26 molecules of chlorine reacting per absorbed quantum of light. The temperature coefficient of these chlorinations was not investigated, except for benzene, for which reaction Slator [114] determined a value of 1.5.

Chlorination of Aliphatic Compounds. Benrath and Hertel [115] studied the chlorination of saturated aliphatic compounds dissolved in carbon tetrachloride. An induction period was observed, being shorter for purer substances. This induction period is possibly due

[109] *Z. physik. Chem.*, 45, 540 (1903).
[110] *Ibid.*, 56, 43 (1906).
[111] *Ibid.*, 85, 329 (1913).
[112] *Loc. cit.*
[113] *Z. Elektrochem.*, 34, 521 (1923)
[114] *Loc. cit.*
[115] *Z. wiss. Phot.*, 23, 30 (1924).

to the inhibitive effect of oxygen discussed in the preceding section. The kinetics of the different chlorinations were somewhat different; for instance, a unimolecular reaction with respect to chlorine was observed in the case of propionic acid, whereas the rate of reaction with other substances, as for instance with acetic acid, was better expressed by an equation $k \log t = [Cl_2]_0 - [Cl_2]_t$, which lacks a kinetic interpretation. We may note that these latter experimental data of Benrath and Hertel can be at least roughly expressed by the equation of a bimolecular reaction:

$$\frac{d[Cl_2]}{dt} = k\,[Cl_2]\,[C_2O_2H_4]$$

Whereas, in acetic acid, only one hydrogen atom could be substituted by chlorine, the reaction then coming to an end, in propionic and butyric acids two hydrogen atoms were substituted by chlorine and the reaction went in two distinct steps, only the monochlorinated substitution product being formed in the first.

Bromination of Toluene. Luther and Goldberg[116] suggested that the bromination of toluene was not inhibited by oxygen, but Bruner and Czernecki[117] demonstrated that inhibition by oxygen was also characteristic of the photochemical bromination of toluene. The inhibitive effect of oxygen is reduced if iodine is present in the solution, the iodine probably reacting with oxygen to form oxyiodine compounds. In absence of oxygen, the rate of reaction is proportional to the incident light intensity and to the concentration of toluene, being independent of the bromine concentration if the absorption of light by this latter is complete. The bromination occurs in the side chain and has a high temperature coefficient, 1.8, whereas the thermal reaction shows a still higher value, 4.0. Bodenstein[118] estimated the quantum yield of this reaction to be as high as 10^6 in absence of oxygen. He suggested further that the temperature coefficient of the light reaction indicates the activation energy which a toluene molecule must possess in order to react and that therefore, in the thermal reaction, which has a still higher value, the surplus: $^4{}^0/_{1.8} = 2.2$ is related with the activation of bromine necessary for the thermal reaction to take place. The bromination of toluene was also studied by Andrich and Le-Blanc,[119] who observed an oxidation of the hydrogen bromide formed by oxygen present in the system.

They noticed also that light of shorter wave length than about

[116] *Loc. cit.*
[117] *Bull. Acad. Sci. Cracow* (A) 576 (1910).
[118] *Z. physik. Chem.*, 85, 297 (1913).
[119] *Z. Elektrochem.*, 20, 543 (1914); *Z. wiss. Phot.*, 15, 148 (1915).

3500 Å. was ineffective in causing a reaction, though it was strongly absorbed by the solution of bromine in toluene. A comparison of the absorption spectra showed that toluene alone absorbs light only below 3000 Å., that bromine dissolved in hexane has a pronounced minimum of absorption at about 3200 Å.,[120] but that a solution of bromine in toluene shows no minimum, the absorptive capacity uniformly increasing towards shorter wave lengths. The authors suggest that the change in the absorption spectrum of bromine is due to a formation of molecular compounds with toluene, these absorbing the ultraviolet rays, but not reacting. In support of their view, Andrich and LeBlanc demonstrated that bromination of hexane was sensitive to all wave lengths absorbed by bromine, in agreement with the normal absorption spectrum of this solution of bromine.

In the experiments of Andrich and LeBlanc it was found that bromine reacted with toluene *after* an illumination by short ultraviolet rays, a catalyst being apparently formed by the action of these rays. This effect not being very reproducible, was not studied quantitatively.

Plotnikoff[121] enumerates a large number of brominations of compounds with double bonded carbon atoms and reports the results of a kinetic study on the bromination of α-phenyl-cinnamic-acid nitrile: $\begin{matrix} C_6H_5 \\ H \end{matrix}\!\!\diagdown\!\!\diagup C{:}C\!\!\diagup\!\!\diagdown \begin{matrix} COOH \\ CN \end{matrix}$ in monochromatic light, 4360 Å. The reaction was studied in carbon tetrachloride solution at 7°. The bromination product being unstable at this temperature, a dark-light stationary state is reached, for which Plotnikoff derives the equation:

$$K = I_0 \frac{(1-e^{-i[Br_2]})^2\,[C_1]}{[C_1Br_2]}$$

where $[Br_2]$, $[C_1]$ and $[C_1Br_2]$ are the concentrations of bromine, of nitrile and of the bromination product and i is the light absorption constant of bromine.

Plotnikoff's measurements apparently confirm this equation, but even after 8 hours of illumination, the stationary state was far from being reached, an extrapolation being probably used for its determination. No experiments to reach the stationary state from the other side were reported. A short calculation shows that the initial rate of bromination, when only negligible amounts of the reaction product are present, does not follow the kinetic equation which can be deduced from Plotnikoff's equation of the stationary state. Finally,

[120] Comp. also Coehn and Stuckard, who find a similar absorption minimum in gaseous bromine, *Z. physik. Chem.*, 91, 722 (1916).
[121] *Z. wiss. Phot.*, 19. 1 (1919).

Berthoud [122] obtained different experimental results with respect to the stationary state equation. Under these circumstances a discussion of the theoretical foundations of Plotnikoff's equation would be fruitless. The experiments of Berthoud and Nicolet indicate that the stationary state can be represented by the equation:

$$\frac{[Br_2]\,(k_1\,[C_1] + k_2\,[C_1Br_2])}{[C_1Br_2]} = K.$$

The constant K was found to be independent of the light intensity. In agreement with this observation, Berthoud and Nicolet found that the decomposition of the brominated nitrile is not a thermal reaction, as was assumed by Plotnikoff, but is photosensitised by bromine.

Berthoud further affirms that, light absorption by bromine being complete, the rate of bromination is represented by the equation:

$$+\frac{d\,[C_1Br_2]}{dt} = k\sqrt{I_0}\,[Br_2]$$

if the concentration of the bromination product is small. The opposed reaction according to Berthoud follows the equation:

$$-\frac{d\,[C_1Br_2]}{dt} = k'\sqrt{I_0}\,\frac{[C_1Br_2]}{[C_1]}$$

Berthoud interprets these equations, in which the square root of light intensity is included, in terms of a mechanism which is very similar to that proposed by Berthoud and Bellenot for the reaction of bromine with oxalate ion. The primary dissociation of bromine into atoms and the subsequent reactions of these latter with nitrile and with the bromination product are its main features.

Ghosh and Purkayestha [123] measured the quantum yield of the reactions of bromine with cinnamic acid and with stilbene, obtaining values of about 400 and 300 molecules of bromine reacting per absorbed quantum. Berthoud and Beraneck [124] obtained for these reactions a much lower yield of about 20 molecules. Berthoud asserts that both reactions follow the equation:

$$\frac{d\,[ABr_2]}{dt} = k\sqrt{I_0}\,[Br_2]$$

if the light absorption is complete and the equation

$$\frac{d\,[ABr_2]}{dt} = k\sqrt{I_0}\,\sqrt{[Br_2]^3}$$

if light is only slightly absorbed by bromine. ($[ABr_2]$ denotes the bromination product.) The large variation in the quantum yield

[122] *Trans. Farad. Soc.*, 21, 554 (1925).
[123] *Quart. J. Indian Chem. Soc.*, 2, 261 (1925).
[124] Berthoud, *loc. cit.*

obtained by different investigators supports, of course, the suggestion that the reaction velocity is not proportional to the light intensity. Berthoud again introduces bromine atoms as the primary product of light action. The suggested mechanism of both reactions:

$$\begin{aligned}
&(1)\quad Br_2 + h\nu \longrightarrow 2Br\\
&(2)\quad A + Br \longrightarrow ABr\\
&(3)\quad ABr + Br_2 \longrightarrow ABr_2 + Br\\
&(4)\quad 2ABr \longrightarrow 2A + Br_2 \text{ or } \longrightarrow ABr_2 + A
\end{aligned}$$

will account qualitatively for the observed high quantum yield and, at the same time, will lead to kinetic equations which were found to represent the experimental results.

Certain of the photochemical brominations are complicated by the presence of after effects, which are apparently of a nature different from those observed by Berthoud and Bellenot in the reaction of iodine with oxalate ion.

For instance, Mukerji and Dhar [125] find that the ratios of the thermal reactions before and after an illumination are different from unity in such brominations as that of malic, tartaric, lactic and other acids. Probably, light promotes the formation of catalysts here which are active for longer time intervals in the dark.

Summarising our discussion of those chain reactions in which halogens are the light-absorbing component, it is interesting to note the definite trend noticeable in all recent investigations, to explain the observed reaction kinetics by mechanisms in which a primary formation of halogen atoms is postulated. This treatment, besides being in agreement with those theoretical considerations of Franck which were discussed on some of the preceding pages, has already recorded, as we have seen, many definite successes. It can be hoped that, in the near future, this treatment will be extended to other photochemical reactions of halogens, since, of course, only in extreme cases will the primary effect of light on halogens be dependent on other components of the system. It can therefore be hoped that the various experimentally determined kinetics of different reactions will be explained, not by postulating a specific light action on halogens for every case studied, but by considering the different reactions of primarily formed halogen atoms, which are determined only by the chemical nature of the other substances present in the system. One process where certainly no formation of halogen atoms can be expected is the action of short ultraviolet rays on bromine in toluene. But then, as we have seen, the absorption spectrum of bromine is

[125] *Quart. J. Indian Chem. Soc.*, **2**, 277 (1925).

materially changed by this solvent, indicating a formation of some molecular compounds. It can be expected that all the above-mentioned "extreme cases" will be found to be due to similar causes. Experimental study can indicate their presence independently of kinetic measurements, since the formation of compounds is usually manifested by a marked change in the absorption spectra of the halogens. From the survey of the chain reactions given, it might be concluded that all these are reactions in which halogens take part. This is by no means correct. Many reactions in liquid phase are known which possess all the characteristics of a chain reaction and in which halogens are not involved.

Henri and Wurmser [126] showed that the hydrolysis of acetone is a chain reaction, as many as 200 molecules reacting per absorbed quantum of ultraviolet light. Baly,[127] in connection with this observation suggested that the equivalence law was in general not applicable to reactions in solutions, since a part of the necessary reaction energy is supplied by the solvent whose action consists, in the opinion of Baly, in opening up the electric fields of force of dissolved molecules. Recently, Bowen and Watts [128] criticised the results obtained by Henri and Wurmser, suggesting that they were due to a considerable unsuspected evaporation of acetone. Bowen and Watts find, on the contrary, a much slower reaction of acetone than would be anticipated from the equivalence law. The not very exact experimental method of Bowen and Watts indicates that their criticism may not be entirely sound.

Besides acetone hydrolysis, such reactions as the decomposition of ozone in ultraviolet and visible light, the decomposition of hydrogen peroxide, the oxidations of hydriodic acid, of sulfites, of iodoform and several others must be enumerated among chain reactions. Besides an excessive quantum yield observed in many of these reactions, they possess another property common to chain reactions. We have repeatedly observed that those reactions which have an exceedingly large quantum yield are particularly sensitive to the presence of even small traces of foreign substances, the presence of which either accelerates or retards the rate of these reactions. Such sensitivity to catalysts and inhibitors and, also, a dependence of the rate of reaction on the solvent used, is particularly pronounced in all of the chain reactions enumerated above. In fact, some of these reactions were studied most exhaustively with respect to catalytic action, whereas

[126] *Compt. rend.*, **156**, 1012 (1913).
[127] *Physik. Z.*, **14**, 893 (1913).
[128] *J. Chem. Soc.*, **127**, 1607 (1925).

little attention was paid to the kinetics of the non-catalysed reaction, this being sometimes experimentally unrealisable. In view of these circumstances it appears desirable to discuss first the so-called photo-sensitised reactions, among which we shall find reactions showing the simple characteristics predicted by the equivalence law, as well as cases of chain reactions. We shall then undertake in a succeeding chapter the discussion of catalytic phenomena.

CHAPTER IV

PHOTOSENSITISATION

We have already met, among the many reactions described, a few examples of processes in which the light absorbing component, remaining itself apparently unchanged, induces reaction of other substances present. For instance, the action of chlorine on the decomposition of sulfuryl chloride and of phosgene and in the synthesis of water are examples of this kind.

In course of time, a large variety of photochemical reactions were discovered, reactions which, being in themselves insensitive to light of a particular spectral region could be made sensitive if a suitable substance—a sensitiser—absorbing light of the desired spectral region, was added to the system. In dealing with these photosensitised reactions two main problems are met; it is of interest to learn what are the kinetics of the induced reactions and what is the mechanism of the photosensitisation itself. The latter problem is particularly important, since we shall find the kinetics of photosensitised reactions, as would be expected, not markedly different from the kinetics of the reactions we have dealt with thus far.

At first glance we might be tempted to suggest that photosensitisation is a kind of chemical catalysis and try to interpret it in terms of the different theories of the latter. On closer investigation, we find, however, that the photosensitising action must be different in its nature from catalysis, as not only spontaneous reactions, but also those involving an increase in the free energy of the system can be realised by introduction of suitable photosensitisers.

As early as 1873, Vogel [1] discovered that photographic plates could be sensitised to green and even to red light by treating them with certain dyestuffs. Since then, various photosensitised reactions have been discovered in all branches of photochemistry and many theories of the processes advanced. In our treatment of the subject we shall depart from the historical point of view and start with a reaction, which, although studied only in recent years, is, by now, due mostly to physical researches, the only case of photosensitisation, the mechanism of which can be regarded as fully established.

[1] *Ber.*, **6**, 1305 (1873).

Photosensitisation by Excited Mercury

It has been known for a long time that mercury vapour emits fluorescence radiation when illuminated by the light of a cooled mercury lamp. This phenomenon becomes particularly simple when vapour at low pressures is used and the mercury line 2536.7 Å. is used as the light source. This line is extraordinarily strongly absorbed by mercury vapour. The intensity of incident light is decreased to one-half by a layer of vapour only a few mm. deep even at 10^{-3} mm. pressure. However, cold mercury vapour absorbs only the central portion of the line, so that as a light source a cooled mercury arc must be used, since otherwise the 2536.7 Å. line is broadened and self-reversed.

With low pressures of mercury vapour, the fluorescence radiation consists only of the line 2536.7 Å., being thus a resonance fluorescence. This was explained, on the basis of Bohr's theory, by assuming that mercury atoms in the normal quantum state absorb light of the frequency 2536.7 Å. and that the resulting excited atoms can lose their excess quantum energy by reradiation only in one way: by returning to the normal quantum state. The spectroscopic studies of the mercury spectrum resulting in the above explanation of the resonance fluorescence permitted a calculation that the mean life of excited mercury atoms was about 10^{-7} sec.

Wood [2] noticed that the intensity of mercury vapour fluorescence was decreased by adding some air to the illuminated vapour. Franck,[3] extending Klein and Rosseland's [4] theory on inelastic collisions between atoms and electrons to collisions between atoms, pointed out that, from the thermodynamical point of view, a fraction of the collisions between excited and normal atoms must result in a transformation of the quantum energy (of excitation) into the kinetic energy of atomic motion (so-called collisions of the 2nd kind), since the reverse process (collisions of the 1st kind) is actually known to take place.

Recently, Stuart [5] was able to demonstrate that the weakening of mercury fluorescence is quantitatively accounted for by the loss of excitation energy on inelastic collisions between excited mercury atoms and foreign gas molecules. Stuart further showed, in agreement with earlier observers, that the yield of inelastic collisions is widely different for different gases. In the following table, Stuart's

[2] *Physik. Z.*, 13, 353 (1912).
[3] *Z. Physik*, 9, 259 (1922).
[4] *Ibid.*, 4, 46 (1921).
[5] *Ibid.*, 32, 262 (1925).

results are represented, the second column indicating the pressure of the gas at which the mercury vapour fluorescence is reduced to one-half value, in the third column being given the yields of inelastic collisions as a fraction of the total number of collisions. These are calculated from the "one-half value" pressures for assumed molecular radii. A special calculation showed that the radius of an excited mercury atom is probably about three times larger than that of a normal atom.

TABLE 19.

Gas	O_2	H_2	CO	CO_2	H_2O	N_2	Ar	He
Half value pressure in mm.	0.35	0.20	0.40	2.0	4.0	30.0	240.	760
Yield of inelastic collisions	1.00	0.70	0.80	0.20	0.10	0.013	0.002	0.0003

A more intimate knowledge of the processes involved in the collisions of the second kind can be obtained from the studies of Cario [6] and Cario and Franck.[7] These authors showed that in a mixture of mercury and thallium vapours illuminated by the line 2536.7 Å., absorbed only by mercury, fluorescence light is emitted also by thallium. However, practically only those lines were observed the quantum energy of which is less than 112,000 cal. (the energy of the mercury line 2536.7 Å.) and, moreover, the thallium lines were unusually broadened, indicating a high kinetic energy of the light-emitting atoms. The very reasonable explanation of these observations given by the authors is that, on collision of an excited mercury atom with a normal atom of thallium, a twofold process takes place: a fraction of the excitation energy of mercury is taken up by the thallium atom in the form of excitation energy and the surplus is distributed between the two atoms in the form of translational energy according to the usual laws governing collisions between two bodies.

Knowledge of the fact that the excitation energy of an atom can be transmitted to the colliding body either in the form of intramolecular energy or be transformed into kinetic energy of atom movements (heat energy) and that both processes can take place simultaneously, will enable us to understand more clearly the nature of several chemical processes, which, as will now be shown, are due also to the action of excited mercury atoms.

Photosensitised Formation of Atomic Hydrogen. Cario and Franck,[8] studying the action of excited mercury atoms on hydrogen,

[6] *Z. Physik*, 10, 185 (1922).
[7] *Ibid.*, 17, 202 (1923).
[8] *Ibid.*, 11, 161 (1922).

observed a gradual removal of this latter from the gas phase. Apparently a clean-up of hydrogen on the walls of the vessel took place. A more rapid decrease in pressure was observed when different metallic oxides, such as tungsten oxide, were introduced into the reaction vessel. Simultaneously, a reduction of the oxides and a formation of water was observed. Cario and Franck suggested that a dissociation of hydrogen into atoms took place on collisions with excited mercury atoms. Since the heat of dissociation of hydrogen is about 101,000 cal., the quantum energy of mercury excitation is sufficient for this process and the surplus—about 11,000 cal.—is probably distributed among the three resulting atoms as kinetic energy. The clean-up of hydrogen on the walls of the vessel and the reduction of such metallic oxides as tungsten oxide are in harmony with this suggestion, since both these effects have previously been described by Langmuir [9] as characteristic of hydrogen atoms thermally produced.

The formation of hydrogen atoms by excited mercury was subsequently decisively demonstrated by Senftleben,[10] who showed that the heat conductivity of a hydrogen-mercury vapour mixture was increased on illumination by the light 2536.7 Å. This effect cannot be explained by the assumption that "hot" or excited hydrogen molecules are formed on collisions with excited mercury atoms. Cario and Franck's observations indicate that, at low pressures, the rate of removal of hydrogen is dependent on the pressure, but that a limiting value is reached for pressures above about 10 mm. Let us consider the kinetics of the processes occurring:

$$\begin{aligned} \mathrm{Hg} + h\nu &\rightarrow \mathrm{Hg}' && (k) \\ \mathrm{Hg}' &\rightarrow \mathrm{Hg} + h\nu && (k_1) \\ \mathrm{Hg}' + \mathrm{H_2} &\rightarrow \mathrm{Hg} + 2\mathrm{H} && (k_2). \end{aligned}$$

The rate of activation and deactivation of mercury will be given by the following equations:

$$(1)\quad +\frac{d\,[\mathrm{Hg}']}{dt} = k; \qquad (2)\quad -\frac{d\,[\mathrm{Hg}']}{dt} = k_1\,[\mathrm{Hg}'] + k_2\,[\mathrm{Hg}']\,[\mathrm{H_2}]$$

$$(3)\quad [\mathrm{Hg}'] = \frac{k}{k_1 + k_2\,[\mathrm{H_2}]}$$

The rate of formation of hydrogen atoms follows now from the equation:

$$(4)\quad +\frac{d\,[2\mathrm{H}]}{dt} = k_2\,[\mathrm{Hg}']\,[\mathrm{H_2}] = \frac{k.k_2\,[\mathrm{H_2}]}{k_1 + k_2\,[\mathrm{H_2}]}$$

which shows, in agreement with Cario and Franck's observations, that, at higher pressures of hydrogen, practically all excited mercury

[9] *J. Am. Chem. Soc.*, **34**, 860, 1310 (1912); **35**, 105 (1913); **36**, 1708 (1914); **37**, 417, 1139 (1915); **38**, 1145 (1916).
[10] *Z. Physik*, **33**, 871 (1925).

atoms will transmit their energy to hydrogen molecules. Per quantum of light energy absorbed two hydrogen atoms will thus be formed.

The above equation represents quite generally the rate of deactivation of excited mercury atoms on collision and Stuart [11] succeeded in showing that the constant k_2 of this equation is very close to the kinetic number of collisions between excited mercury atoms and such gases (compare Table 19, page 127) as oxygen, hydrogen, and carbon monoxide. No direct determination of the rate of hydrogen atom formation has so far been undertaken, but it is quite probable that each inelastic collision of hydrogen and excited mercury is effective in this respect.

Since the first observations by Cario and Franck, extensive work on the reactions of hydrogen atoms produced by excited mercury has been accomplished. Dickinson [12] and later Mitchell [13] demonstrated that when mixtures of hydrogen, oxygen and mercury vapour were illuminated by the line 2536.7 Å., water was formed. They ascribed this reaction to the hydrogen atoms produced. Their experiments were carried out with low pressures of reacting gases.

Taylor and Marshall [14] studied the reactions of hydrogen atoms, produced by inelastic collisions of molecular hydrogen with excited mercury, at atmospheric pressure and demonstrated that rapid reaction occurred with ethylene, ethane being formed. With hydrogen in excess, the rate of this reaction is almost independent of the ethylene pressure. A slower reaction occurred with oxygen, with carbon monoxide (formaldehyde being formed) and with nitrous oxide. No reaction could be observed with carbon dioxide and with nitrogen. This last observation is not in accord with the experiments of W. A. Noyes, Jr.,[15] who obtained traces of ammonia as the product of interaction of hydrogen and nitrogen in presence of hot mercury vapour. This formation of ammonia is exceedingly improbable at ordinary temperatures.

Cario and Franck,[16] discussing the rapid reaction of hydrogen atoms with metallic oxides had suggested that a chain reaction was involved in this process. Taylor [17] came to the same conclusion after estimating the number of absorbed quanta and of molecules reacting.

[11] *Loc. cit.*
[12] *Proc. Nat. Acad. Sci.*, 10, 409 (1924).
[13] *Ibid.*, 11, 458 (1925).
[14] *Trans. Farad. Soc.*, 21, 560 (1925).
J. Phys. Chem., 29, 1140 (1925).
[15] *J. Am. Chem. Soc.*, 47, 1003 (1925).
[16] *Loc. cit.*
[17] *Trans. Farad. Soc.*, 21, 560 (1925).

He suggested that, with ethylene, the chain consists probably of the following reactions

$$C_2H_4 + H \rightarrow C_2H_5$$
$$C_2H_5 + H_2 \rightarrow C_2H_6 + H, \text{ etc.}$$

Marshall [18, 19] studied more quantitatively the reaction of hydrogen with oxygen. The rate of reaction is, at least roughly, represented by the equation:

$$\frac{d[H_2O]}{dt} = k\frac{[H_2]}{[H_2] + [O_2]}$$

which indicates that only hydrogen can be activated for this reaction by collisions with excited mercury. The rate of reaction is also practically independent of the temperature, if the variation in light absorption due to varying mercury vapour pressure is taken into account.

Taylor had suggested [20] that the following reactions take place primarily in the illuminated mixture:

$$Hg + h\nu \rightarrow Hg'$$
$$Hg' + H_2 \rightarrow Hg + 2H$$
$$H + O_2 \rightarrow HO_2$$
$$HO_2 + H_2 \rightarrow H_2O_2 + H, \text{ etc.}$$

This scheme indicates the formation of hydrogen peroxide as primary product. He suggested that the formation of water, observed by earlier investigators, is due to a secondary decomposition of hydrogen peroxide, partly in interaction with mercury present, partly by the action of ultraviolet light.

Marshall succeeded in demonstrating that, by passing a rapid stream of hydrogen and oxygen, saturated with mercury, through the illuminated reaction vessel, the secondary decomposition of hydrogen peroxide could be avoided and an almost 100 per cent yield of this latter be obtained.[21] Marshall's measurements of the quantum yield indicate that more than 4 molecules of hydrogen peroxide are formed by each excited mercury atom, thus supporting the suggested chain mechanism. Marshall's observation that a dilution of the reacting gases with helium or nitrogen hardly affects the yield of reaction is of interest. This is interpreted with the aid of Stuart's observations that the yield of inelastic collisions of mercury with these gases is very small. Marshall's studies on hydrogen peroxide formation and especially the marked parallelism of all the reactions described with those effects, which, according to Bonhoeffer,[22] are characteristic of hydrogen atoms produced by a high tension electric discharge of

[18] *J. Phys. Chem.*, 30, 34 (1926); *ibid.*, 30, 1078 (1926).
[19] See also Bonhoeffer and Loeb, *Z. physik. Chem.*, 119, 474 (1926).
[20] *Loc. cit.*
[21] See also, Taylor, *J. Am. Chem. Soc.*, 48, 2840 (1926).
[22] *Z. Elektrochem.*, 31, 521 (1925) and other publications.

Wood's type, are undoubtedly favourable to the suggestion that hydrogen atoms are the primary product of the collisions between hydrogen and excited mercury atoms. We may note that the view Rideal and Hirst [23] recently advanced that excited hydrogen molecules are the product of interaction with excited mercury would meet serious difficulties in explaining all these effects.

Less convincing in this respect are the observations of Olsen and Meyer [24] on the interaction of low pressure hydrogen and ethylene in presence of excited mercury. They consider the observation that the rate of reaction is approximately proportional to the square root of hydrogen concentration as direct evidence for the presence of hydrogen atoms. Olsen and Meyer suggest that this form of relation is due to a varying rate of diffusion of hydrogen atoms into the reaction vessel from the thin gas layer on the illuminated side, where the absorption of the line 2536.7 Å. by mercury and subsequent formation of hydrogen atoms take place. We shall see later that, in the gas mixture studied, the excited mercury atoms cause not only the production of hydrogen atoms but also several other reactions of varying relative rates. These reactions have not been separately studied by Olsen and Meyer. It is therefore quite possible that the square root proportionality—observed, at that, only over a narrow range of concentrations—has no kinetic meaning and is simulated by the circumstance that the measured pressure change is the result of several competitive reactions. These may be differently influenced by the concentrations of the reactants and still their observed combined effect on pressure can appear to be approximately proportional to the square root of concentration of one of the reactants.[25]

Sensitised Ozone Formation. So far, only those reactions have been considered which in presence of excited mercury atoms involve a primary formation of hydrogen atoms. Recent investigations have decisively demonstrated that the photosensitising action of excited mercury atoms is not limited to hydrogen molecules, but that, varying the gases present, a large variety of photochemical reactions can be secured as a result of this photosensitising action.

Dickinson and Sherrill [26] showed that ozone is formed if an oxygen-mercury vapour mixture is illuminated by the light 2536.7 Å. Dickinson and Sherrill suggest that, since the quantum energy of mercury excitation is insufficient for the dissociation of oxygen into atoms,

[23] *Nature*, 117, 449 (1926).
[24] *J. Am. Chem. Soc.*, 48, 389 (1926).
[25] See page 170.
[26] *Proc. Nat. Acad. Sci.*, 12, 175 (1926).

excited oxygen molecules must be formed and react with normal molecules to form ozone. The study of this reaction, as well as of hydrogen peroxide formation, is complicated by a simultaneous oxidation of mercury.

Further Mercury-Sensitised Reactions. Senftleben and Rehren [27] studied the photosensitised decomposition of water vapour. They found only hydrogen as gaseous decomposition products, and suggested, therefore, that the reaction proceeds in the following steps:

$$Hg' + H_2O \rightarrow Hg + H + OH$$
$$2OH \rightarrow H_2O_2.$$

This reaction scheme assumes that the energy of an O—H linkage is less than 112,000 cal. and Senftleben [28] subsequently based, on this assumption, interesting considerations concerning the electron affinity of oxygen.

Earlier experiments of Taylor and Marshall [29] had already indicated that, in a hydrogen-ethylene mixture, in addition to the hydrogenation of this latter to ethane, its polymerisation occurs from the action of excited mercury atoms.

Olsen and Meyer [30] observed an initial increase in pressure in a hydrogen-ethylene mixture, followed by a decrease. The initial rise was smaller for hydrogen-rich mixtures. They suggested that, in presence of excited mercury atoms, three processes take place: hydrogenation of ethylene by hydrogen atoms, its decomposition and its polymerisation due to collisions with excited mercury.

The experiments of Bates and Taylor [31] indicate that ethylene is decomposed to acetylene and this latter readily polymerised by the action of excited mercury. The reaction is further complicated by a formation of organic mercury compounds and this removal of mercury atoms from the gas phase explains, according to Taylor, the observations of Rideal and Hirst [32] that the rate of reactions, caused by excited mercury, is decreased with time not only in systems containing oxygen, where a partial oxidation of mercury takes place, but also in hydrocarbon systems.

Taylor suggests that the photosensitised reactions of hydrocarbons involve a chain mechanism and an intermediary formation of free radicals. He supports his view by the experiments of Jones [33] on the

[27] *Z. Physik*, 37, 529 (1926).
[28] *Ibid.*, 37, 539 (1926).
[29] *Ibid.*
[30] *Ibid.*
[31] See: Taylor, *J. Am. Chem. Soc.*, 48, 2840 (1926); *Proc. Am. Phil. Soc.*, 65, 90 (1926).
[32] *Loc. cit.*
[33] See Taylor, *Am. Phil. Soc.*, 65, 90 (1926).

hydrogenation of unsaturated hydrocarbons in presence of decomposing metal alkyls. These experiments show that each metal alkyl molecule which decomposes, probably with formation of free radicals, induces the hydrogenation or condensation of several unsaturated hydrocarbon molecules, thus supporting the view expressed by Taylor.

Recently, Taylor and Bates [84] have demonstrated the wide variety of photochemical reactions which can be induced by the action of excited mercury atoms. The following table represents some of their results. The analysis was extended only to those products of reactions which are not condensed in a liquid air trap.

TABLE 20.

Substance	Ratio of photosensitised to non-photosensitised rate of reaction	Analysis of gaseous products of the non-photosensitised reaction	Analysis of gaseous products of the photosensitised reaction
H_2O			73% H_2; 27% O_2
NH_3	200:1	96% H_2; 4% N_2	89% H_2; 11% N_2
C_2H_4			88% H_2; 12% CH_4 etc.
CH_3OH	600:1		58% H_2; 42% CH_4 + CO
C_2H_5OH	50:1		46% H_2; 50%CO + CH_4
C_6H_{14}	1000:1		96% H_2; 4% CH_4
C_6H_6	30:1		60% H_2; 40% CH_4
$(CH_3)_2CO$	2:1	100% CO + CH_4	100% CO + CH_4
HCOOH	400:1		76% CO; 24% H_2
$C_2H_5NH_2$	60:1	96% H_2; 4% N_2	96% H_2; 3.7% CH_4; 0.3% N_2

The authors point out that, although the variety of reactions which can be caused by excited mercury is not limited even to the cases studied, it is evident that some substances are more easily destroyed by the collisions with excited mercury atoms than are others. They suggest further that the mechanism of these reactions consists generally in an initial breaking up of one of the linkages C—H; O—H; N—H on collision with excited mercury and that therefore all these linkages possess less energy than 112,000 cal. Taylor and Bates draw attention, further, to the fact that the gaseous products of ammonia decomposition are not in the stoichiometric ratio (75 per cent H_2; 25 per cent N_2). This observation supports the view expressed that the primary reaction consists in the breaking up of an ammonia molecule into hydrogen atom and the radical NH_2. The authors suggest that in the course of reaction, the groups NH_2 combine to hydrazine. They find actually some indications of the presence of this latter substance in the condensable reaction products.

[84] *Proc. Nat. Acad. Sci.*, 12, 714 (1926); *J. Am. Chem. Soc.*, 49, 2438 (1927); also, Dickinson and Mitchell, *Proc. Nat. Acad. Sci.*, 12, 692 (1926).

An extension of these experiments, including a complete analysis of the reaction products and kinetic studies on the rate of reactions, undoubtedly promises even more interesting results for the general theory of chemical kinetics, since, for several of these substances, their thermal decompositions and the non-photosensitised photochemical reactions have already been the object of quantitative study. In the thermal reactions—as calculated from the temperature coefficients—smaller amounts of activation energy cause a decomposition, whereas the non-sensitised photochemical decompositions require in several of the cases now studied by Taylor and Bates, even larger energy quantas than those of excited mercury atoms. A quantitative comparison of the reaction kinetics and especially of the decomposition products of the same molecule, but in reactions caused by these varying amounts of activation energy, will be a valuable contribution to our knowledge of molecular structure and of the processes involved in collisions of molecules and in absorption of light quanta by them. The study of these photosensitised reactions is only in its beginning, but it is and will be greatly helped by the amount of information available on the primary processes which follow the absorption of light quanta by mercury atoms. We have seen that excited mercury atoms either re-emit their excess quantum energy as radiation, or dissipate it in the form of heat energy, or, finally, transmit this energy to other molecules in a form which causes a chemical change in these latter. We have also seen that the relative rates of these three processes and the nature of the subsequent chemical reaction depend on the composition (i.e., on the concentrations of the components) of the system in a way which directly follows from the theory proposed.

Photosensitisation by Chlorine

From the theoretical standpoint, the study of photosensitisation by chlorine is in a less developed state. The few examples of this process, which we have met in preceding chapters, were not suited to a thorough discussion, since the photosensitised reaction was in all cases superposed on other processes of rather complicated kinetic relations, lacking, so far, complete theoretical explanation.

The Sensitised Decomposition of Ozone. A classical example of photosensitisation by chlorine is the decomposition of ozone. This latter possesses absorption bands situated in the ultraviolet and in the red-yellow part of the visible spectrum. Studies of the kinetics of the decomposition of ozone under the influence of these wave lengths

indicate a chain reaction of a character not yet fully established which will be dealt with in the next chapter. It suffices now to remark that the rate of reaction is dependent on the ozone concentration and is also a function of the concentrations of other gases present in the system.

The entirely different kinetic relations found by Weigert [35] in the decomposition of ozone photosensitised by chlorine are very remarkable. He observed that the rate of ozone decomposition in a mixture with chlorine, illuminated by light absorbed only by this latter, is entirely independent of the ozone concentration in the limits 5-0.1 per cent ozone in mixtures at atmospheric pressure. Weigert [36] further demonstrated that the rate of ozone decomposition is proportional to the amount of light energy absorbed by the chlorine. In agreement with an earlier estimate of Bodenstein,[37] Bonhoeffer [38] found the quantum yield of this reaction in the light of the mercury lines 4360 Å. and 4050 Å. to be equal to 2. Bonhoeffer also confirmed Weigert's observation that the rate of reaction is independent of the ozone concentration.

In attempting to explain the reaction mechanism, Bonhoeffer suggested that activated chlorine molecules were formed on light absorption and that they transmitted their energy on collisions to ozone The reactions were supposed to occur either by

$$\text{I} \quad \begin{aligned} Cl_2' + O_3 &\rightarrow Cl_2 + O_2 + O \\ O + O_3 &\rightarrow 2O_2 \end{aligned}$$

or by

$$\text{II} \quad \begin{aligned} Cl_2' + O_3 &\rightarrow Cl_2O' + O_2 \\ Cl_2O' + O_3 &\rightarrow Cl_2 + 2O_2. \end{aligned}$$

Both these reaction schemes yield two molecules of ozone per quantum of light absorbed by chlorine if every activated chlorine molecule collides with ozone. Since the reaction velocity is independent of the ozone concentration, Bonhoeffer suggested that the life of activated chlorine is at least 10^{-7} sec. and that, moreover, activated chlorine molecules do not dissipate their surplus energy on collisions with oxygen and chlorine molecules, before they meet ozone molecules.

The Sensitised Decomposition of Chlorine Monoxide. Recently, Bodenstein and Kistiakowsky [39] demonstrated that the photochemical decomposition of chlorine monoxide, studied by Bowen (*loc. cit.*), is also photosensitised by chlorine. The kinetics of this reaction are only

[35] *Ann. Physik*, 24, 243 (1907).
[36] *Z. Elektrochem.*, 19, 840 (1913).
[37] *Ibid.*, 19, 840 (1913).
[38] *Z. Physik*, 13, 94 (1923).
[39] *Z. physik. Chem.*, 116, 371 (1925).

different from those of ozone decomposition inasmuch as chlorine monoxide has an absorption band in the same spectral region as chlorine and the photosensitised reaction is therefore superposed upon the non-sensitised decomposition. The authors demonstrated that the rates of both these reactions of chlorine monoxide in monochromatic light, 4360 Å., were determined by the relative amounts of light energy absorbed by chlorine and by chlorine monoxide and that both reactions, independent of the chlorine monoxide concentration (94 per cent—0.5 per cent), yielded two decomposed molecules per quantum of light energy absorbed. Bodenstein and Kistiakowsky showed also that the admixture of large quantities of oxygen and nitrogen did not change the rate of either reaction in the least. The decomposition of chlorine monoxide does not follow quantitatively the path indicated by the equation

$$2Cl_2O \rightarrow 2Cl_2 + O_2$$

since minute quantities of chlorine dioxide ClO_2 are formed in the photochemical and the thermal reactions. Bodenstein and Kistiakowsky's experiments indicate that, in the photochemical reaction, a stationary concentration of chlorine dioxide is formed on illumination. They considered that this last observation was an indication that the reaction mechanism involved activated molecules. Chlorine as well as chlorine monoxide is supposed to become activated on light absorption and chlorine is supposed to transmit its energy on collisions to chlorine monoxide. All other collisions of activated molecules must be of course elastic, since the rate of reaction is independent of the chlorine monoxide concentration. The decomposition of chlorine monoxide was supposed to occur either by

$$Cl_2O' + Cl_2O \rightarrow 2Cl_2 + O_2 \qquad \text{(main reaction)}$$

or by

$$\left.\begin{array}{ll} 1. & Cl_2O' + Cl_2O \rightarrow ClO_2 + Cl_2 \\ 2. & Cl_2 + ClO_2 \rightarrow 2Cl_2 + O_2 \\ 3. & Cl_2 + Cl_2 \rightarrow 3Cl_2 \end{array}\right\} \text{(side reaction)}$$

This scheme, accounting for the formation of small stationary quantities of chlorine dioxide by a not entirely improbable circle of reactions, is in agreement with experimental results, so long as the assumed remarkable stability of activated molecules against collisions with indifferent molecules is unquestioned. This last assumption was, however, criticised by Allmand [40] in connection with ozone decomposition. Allmand pointed out that, according to Rideal and Norrish,[41] chlorine

[40] *Trans. Farad. Soc.*, 21, 503 (1925).
[41] *Loc. cit.*, page

activates oxygen, water being formed in hydrogen containing systems, and that, therefore, collisions of activated chlorine with oxygen cannot be elastic. Allmand further demonstrated that, assuming an activation of oxygen to take place, but neglecting the degradation of energy on mutual collisions between oxygen and between chlorine molecules, an equation for the rate of ozone decomposition can be derived which is in agreement with Weigert's and Bonhoeffer's experiments. This theory will, of course, account also for the decomposition of chlorine monoxide, if the assumption be made that neither chlorine nor oxygen molecules lose their activation energy on collisions with nitrogen. Using the data contained in the paper of Bodenstein and Kistiakowsky, we can estimate that the yield of inelastic collisions with nitrogen must be smaller than 0.001 both for chlorine and for oxygen. This is a very small value, if compared with the yield of inelastic collisions of excited mercury with nitrogen molecules.

Weigert's Theory of Isochromatic Fluorescence. An entirely different theory, developed to account for all chlorine reactions, was advanced by Weigert.[42] He suggests that chlorine is capable of emitting the absorbed light energy in the form of isochromatic radiation, thus possessing the property of resonance fluorescence over its whole continuous absorption spectrum. The emitted radiation is then absorbed by other chlorine molecules according to Weigert and the process repeated until the light quantum is absorbed by ozone molecules or by chlorine in close proximity to ozone molecules.

This theory, avoiding the difficulties of the suggestions on the kinetics of chlorine photosensitisation earlier discussed, is, however, not free from other objections. First of all, the way in which ozone is brought into active state on illumination with blue light in presence of chlorine must be different from the process of direct absorption of light energy by ozone molecules. Otherwise, no relevant explanation can be offered as to why the reactions caused by ultraviolet and by yellow-red light, and thus by energy quanta both larger and smaller than those of blue light, have both almost identical kinetics of complicated chain character (even in presence of chlorine) [43] but differ so fundamentally from the reaction studied originally by Weigert.

Another difficulty arises from the calculation of Weigert, namely, that as many as 10^4 emission and absorption processes by chlorine must precede the absorption of a light quantum of blue light by ozone. The circumstance by which a light quantum is retained all this time

[42] *Z. physik. Chem.*, 106, 407 (1923).
[43] Kistiakowsky, *Z. physik. Chem.*, 117, 337 (1925).

in the reaction vessel is left unexplained by Weigert. According to Weigert's theory, no proportionality of the reaction rate and light energy absorbed can be expected in differently shaped vessels. Of course, the quantum yield of 2 molecules per quantum is also largely dependent on the size of the vessel.

In support of his theory, Weigert considers the so-called Budde [44] effect. Budde observed a pressure increase on illuminating chlorine with rays absorbed by this latter. More recent investigators have demonstrated that this effect is due to the warming up of chlorine by absorbed light energy and found further that, in very pure and dry chlorine, the Budde effect is very greatly diminished. Weigert explained this observation by suggesting that, in pure chlorine, the total absorbed light energy is emitted again as resonance radiation, whereas presence of moisture causes a transformation of the radiant energy into heat energy. Similarly, in a dry chlorine-hydrogen mixture, absorbed light energy is emitted by chlorine as fluorescence and only presence of moisture makes possible a reaction (see page 86). Recent investigations of the Budde effect in bromine seem further to support Weigert's theory.

Ludlam [45] and later Lewis and Rideal,[46] who studied the Budde effect of bromine, are in agreement that, in absence of water vapour, the effect is very small and therefore they suggest the re-emission of absorbed radiation. Lewis and Rideal find that the intensity of the Budde effect is proportional to the concentrations of bromine and of water vapour and conclude that a hydrate ($Br_2.H_2O$) is formed, which is the photosensitive constituent. They find, further, that the absorption of light by dry bromine begins at shorter wave lengths than that of wet vapour, and ascribe the light absorption in the region 6100-5700 Å. mainly to the bromine hydrate. A calculation of the concentration of the hydrate, yielding values in the range 10^{-11} mols per liter, shows that the light absorption coefficient of bromine hydrate must be extraordinarily high, about 10^7, for the region 5600-5500 Å. The very careful determinations of the light absorption of dry and of wet chlorine by von Halban and Siedentopf [47] established the fact that light absorptions is, in both cases, identical. On the other hand, Dymond [48] demonstrated that iodine, illuminated by light of its continuous absorption spectral region, does not fluoresce at all.

[44] *J. prakt. Chem.*, 7, 376 (1873); comp. also, Richardson, *Phil. Mag.*, 32, 227 (1891); Shenstone, *J. Chem. Soc.*, 71, 471 (1897); Bevan, *Phil. Trans.*, 202, 90 (1904).
[45] *Proc. Roy. Soc. Edin.*, 34, 197 (1924).
[46] *J. Chem. Soc.*, 128, 583 (1926).
[47] *Z. physik. Chem.*, 103, 71 (1923).
[48] *Z. Physik*, 34, 553 (1925).

Kistiakowsky [49] has recently studied the fluorescence of chlorine on illumination with visible light. He found, using two different methods, that, under all conditions, considerably less than 5 per cent of the absorbed light energy is emitted by chlorine as fluorescence. These experiments were carried out with chlorine prepared by the method of Coehn and Jung (comp. page 86), and thus with gas sufficiently pure to insure its complete photochemical non-reactivity. Further, in confirmation of the experiments of Halban and Siedentopf no appreciable difference in the light absorption of moist and dry chlorine could be detected. These results, combined with observations on Budde effect, indicate, in the opinion of Kistiakowsky, that chlorine molecules are dissociated into atoms on absorption of light quanta of the continuous absorption spectral region irrespective of the presence of water or other foreign molecules. Radiant energy is thus primarily transformed into chemical energy and the warming up of the gas must be due to a secondary process: the recombination of the chlorine atoms to molecules. Kistiakowsky concludes that, unless the observations on Budde effect are incorrect, the rate of this recombination must be catalytically accelerated by moisture. The homogeneous reaction being slow in dry and pure chlorine, the chlorine atoms formed in this case recombine mostly on the walls of the containing vessel which conduct the liberated heat away, preventing, or at least decreasing, the warming up of the gas.

Halogen Atoms as Sensitisers. We have already seen that, in several other chlorine reactions, a primary formation of atoms on light absorption was successfully postulated. In the case of the photosensitised decompositions of ozone and chlorine monoxide, such a mechanism requires the additional postulation of chlorine oxides as intermediary products and a successful theoretical treatment will be possible only after more is known concerning the nature of these unstable compounds. An intermediate formation of chlorine monoxide in the ozone reaction, as suggested by Bonhoeffer, finds considerable support in the observations on the rate of photochemical chlorine monoxide decomposition, but is, on the other hand, difficult to account for if chlorine atoms are assumed to be the primary products of light action. As a partial confirmation of the idea that intermediary products are formed during the sensitised ozone decomposition, the observation of Bonhoeffer (*loc. cit.*) may be mentioned, according to which, in presence of bromine, as many as 30 molecules of ozone are decomposed per quantum of light absorbed by the former. It is

[49] *J. Am. Chem. Soc.*, 49, 2194 (1927).

interesting to compare this result with the observations that whereas a chlorine-ozone mixture in red light reacts slowly to form chlorine hexoxide (Cl_2O_6), a similar mixture with bromine explodes vigourously if 50-60 per cent ozone is used.

Further Photosensitisations

The Sensitised Decomposition of Nitrogen Pentoxide. The third gaseous photosensitised reaction which apparently exhibits simple kinetic relations is the decomposition of nitrogen pentoxide. Daniels and Johnston [50] observed that the decomposition of nitrogen pentoxide was not accelerated by visible or infra-red light, unless some nitrogen dioxide was present. This latter shows a strong light absorption in the blue part of the visible spectrum. In agreement with this fact, Daniels and Johnston found that light of the region 4000-4600 Å. was active in the reaction. Their qualitative experiments indicate, further, that the rate of photosensitised decomposition is proportional to the amount of light energy absorbed by nitrogen dioxide. This can be deduced from the observations of Daniels and Johnston that, at low concentrations of nitrogen dioxide, the rate of reaction is proportional to its amount. At higher concentrations of nitrogen dioxide, Daniels and Johnston find an approximately constant rate of reaction, as would be expected, since nitrogen dioxide possesses a strong absorptive power for light of the spectral region 4000-4600 Å. A rough calculation of the quantum yield, on the basis of the data contained in the paper of Daniels and Johnston, yields an upper limit of about 18 molecules per quantum.

Fazel and Karrer [51] have suggested that the mechanism of this reaction consists in the primary formation of activated nitrogen dioxide molecules and their subsequent collisions with nitrogen pentoxide, resulting in the decomposition of the latter. A more plausible theory of the reaction mechanism, supported by experiments, was recently advanced by Norrish,[52] who showed that nitrogen dioxide is dissociated into oxygen and nitric oxide on absorption of light energy and suggested that nitrogen pentoxide is decomposed in a secondary thermal reaction with nitric oxide according to the equation:

$$NO + N_2O_5 \rightarrow 3NO_2.$$

The Sensitised Oxidation of Carbon Trichlorobromide. Grüss,[53] studying the action of chlorine on carbon trichlorobromide, discovered

[50] *J. Am. Chem. Soc.*, **43**, 72 (1921).
[51] *Ibid.*, **48**, 2837 (1926).
[52] *Nature*, **119**, 123 (1927).
[53] *Z. Elektrochem.*, **29**, 144 (1922).

a reaction of this latter substance, in which bromine plays the rôle of a photosensitiser. Carbon trichlorobromide, illuminated by visible light in presence of bromine and oxygen, undergoes an oxidation, phosgene being formed,

$$2CCl_3Br + O_2 \rightarrow 2COCl_2 + Cl_2 + Br_2.$$

The rate of reaction is proportional to the amount of light energy absorbed by bromine. Variation of the carbon trichlorobromide concentration from the pure substance to a solution of $1CCl_3Br$ in 15 CCl_4 and also variation of the oxygen concentration, at least above about 2.3×10^{-3} mols per liter, are without influence on the rate of reaction. The determination of the quantum yield, carried out in light of the mercury lines 4360 and 4050 Å., yielded about 1 molecule of oxygen reacting per quantum of light absorbed by bromine. This determination must be considered as approximate, since the single values vary from 0.58 to 1.25, but no systematic influence of the concentrations of single reactants is to be discovered in the experimental data. Grüss suggested that activated bromine molecules are formed, as the result of light absorption, and that they activate oxygen on collisions.

Weigert [54] extended his theory of resonance fluorescence as the cause of photosensitisations, to this reaction also. It seems that, as in the cases of ozone and chlorine monoxide decomposition, no decisive conclusions on the mechanism of this photosensitisation by bromine can be drawn at present.

The Sensitised Maleic-Fumaric Acid Transformation. Much more complicated kinetic relations are found in another photosensitisation by bromine in solution. We have noted, in the second chapter, that the isomerisation of maleic to fumaric acid is sensitive to ultraviolet light and that the quantum yield of this reaction is very low.

Wislicenus [55] noticed that, in presence of bromine, maleic acid in aqueous solution was rapidly transformed into fumaric acid on illumination by visible light. An estimate [56] shows that, in this reaction, the quantum yield is larger than unity. A similar reaction of the diethyl ester of maleic acid in carbon tetrachloride solutions was recently studied by Eggert and Borinski [57] and Eggert, Wachholtz and Schmidt.[58] These authors investigated most exhaustively the kinetics not only of the photosensitised isomerisation but also of the bromination of the double carbon bond taking place on illumination. Their results are best represented by a table in which γ_1 indi-

[54] *Loc. cit.*
[55] *Ber. Sachs. Ak. Wiss.*, **47**, 491 (1895).
[56] Eggert, *Physik. Z.*, **25**, 19 (1924).
[57] *Ibid., loc. cit.*
[58] *Physik. Z.*, **26**, 865 (1925).

cates the quantum yield of the isomerisation reaction and γ_2 the yield of the bromination. The transformation of the diethyl maleate ester into fumarate ester is accompanied by a heat evolution of about 7000 cal. The authors investigated also the action of bromine on fumarate ester and found no isomerisation, but only bromination. They state that the kinetics of this reaction are very similar to that of maleate ester.

TABLE 21. *Diethyl maleate ester.*

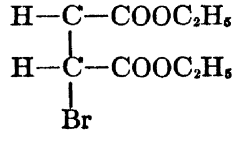
Relation Investigated	γ_1 Isomerisation	γ_2 Bromination
Quantum yield at 21° Light 4360 Å. 0.1 *N* Br_2	295	8.2
Light intensity	γ_1 and γ_2 are independent of the light intensity; the reaction velocity is thus proportional to it. Light intensity varied in the ratio 1:6.	
Concentration of the ester	γ_1 and γ_2 independent of the concentration within the limits, pure ester to 1 mol ester in 70 mols CCl_4.	
Concentration of bromine	γ_1 constant when bromine varied from 0.03 to 0.3 *N*.	γ_2 proportional to bromine concentration.
Wave length	$\frac{\gamma_1\,(4360\text{Å.})}{\gamma_1\,(5460\text{Å.})} = 1.9$	$\frac{\gamma_2\,(4360\text{Å.})}{\gamma_2\,(5460\text{Å.})} = 2.0$
	The ratios are independent of temperature.	
Temperature coefficient	Highly dependent on temperature	
	$\gamma_{24.5°} = 2\gamma_{21.5°}$	$\gamma_{24.5°} = 2\gamma_{15°}$
	$\gamma_{14°} = 1.3\gamma_{4°}$	$\gamma_{15°} = 1.2\gamma_{4°}$

It was also found that the rate of isomerisation decreased when increasing amounts of fumarate ester were added to maleate. Apparently no simple proportionality exists between the relative concentration of the latter and the quantum yield of isomerisation reaction.

An experiment of Schmidt demonstrated that, by illuminating bromine vapour above the surface of the solution, a noticeable reaction in the latter can be realised. This last observation indicates that the primary product of light action on bromine has a life long enough to reach the solution from the gas phase. Eggert considers as most probable the suggestion that excited bromine molecules are primarily formed. They must, of course, have a very long life and be protected against deactivating action of collisions with solvent molecules. Eggert further assumes that, on collision of esters and activated bromine molecules, small amounts of energy are transmitted to the former and activate them. Since the quantum energy of excited bromine mole-

cules is about 65,000 cal. and approximately 300 molecules of ester are activated, a few hundred calories must suffice for the activation of a single ester molecule. After activation the maleate ester is either isomerised—on collisions with indifferent molecules—or brominated on collisions with bromine. The fumarate ester either returns to its normal state or like maleate is brominated (the diethyl ester of dibromosuccinic acid is the product of both brominations). Eggert's theory of activated bromine molecules, giving a formal explanation of the kinetic relations observed, meets, however, extreme difficulties on closer consideration. The assumption that only a few hundred calories are sufficient to activate the ester molecules is particularly improbable, since, at room temperature, already a high percentage of the ester molecules possess this energy according to the statistical energy distribution law and thus a very rapid dark reaction should take place. This is not the case.

Herzfeld [59] pointed out that the difficulties inherent in Eggert's theory can be avoided if a primary formation of bromine atoms and subsequent reactions be assumed. Berthoud [60] also arrived at the same conclusion and suggested as an intermediate stage a compound having trivalent carbon atom



The introduction of bromine atoms as the result of the primary light action and as the cause of the isomerisation and bromination processes requires certain additional hypotheses as to the nature of the chain reactions, since the usual mechanism, including the recombination of the atoms, unavoidably leads to the proportionality of the reaction rate to the square root of absorbed light energy and is thus in disagreement with Wachholtz's experimental results. Another difficulty of the atom chain mechanism is the rapid increase of the quantum yield in light of shorter wave length, which at first sight rather supports Eggert's theory.

Quite recently, Wachholtz [61] worked out Herzfeld's and Berthoud's suggestions to a complete theory of the reaction mechanism and demonstrated that, with some additional assumptions, the above mentioned difficulties can be avoided. The bromine atoms formed are

[59] Comp. a note in Eggert's publication.
[60] *Trans. Farad. Soc.*, 21, 554 (1925).
[61] *Z. physik. Chem.*, 125, 1 (1927).

assumed by Wachholtz to combine with the ester molecules present to yield a short-lived compound (10^{-11} sec.)—a "quasi-molecule." This may be decomposed again under simultaneous isomerisation of the ester molecule or be transformed into a more stable radical of the type suggested by Berthoud. The relative rates of both processes are dependent on the statistical probabilities of corresponding intramolecular changes. If, finally, the unstable intermediary compound collides with a bromine molecule, the diethyl ester of dibromosuccinic acid is formed and a bromine atom is liberated again.

Wachholtz further calculated that, even if only about 0.0001 of all the collisions of bromine atoms and ester molecules lead to the isomerisation of the latter and, correspondingly, only one in a million to the formation of brominated radicals, still the rate of recombination of bromine atoms to molecules (even if occurring on each collision) will be negligible and the rate of reaction will thus be proportional to the light intensity. To obtain full agreement with the kinetic observations it is, however, necessary to assume that the brominated (stable) radicals of maleate (or fumarate) esters do not react with bromine molecules by

$$MBr + Br_2 \rightarrow MBr_2 + Br$$

but only by

$$MBr + MBr \rightarrow MBr_2 + M \text{ or } (MBr)_2$$

or by

$$MBr + Br \rightarrow MBr_2$$

since, otherwise, the bromine atoms would be continuously regenerated in the course of the reactions. This assumption is opposed to the suggestions of Berthoud discussed earlier as to the mechanism of bromination of stilbene and cinnamic acid. These include, as a necessary part of the mechanism, the reactions of the brominated radicals formed with bromine molecules. In the opinion of Wachholtz, the presence of phenyl groups in these last substances can account for the different reactivity of the radicals formed. With regard to the different efficiencies of different wave lengths, Wachholtz assumes that not every absorbed light energy quantum results in the formation of bromine atoms, but that part of the primarily activated bromine molecules lose their energy on collisions of the second kind and the percentage loss is larger for smaller absorbed energy quanta.

The very particular function of the temperature on the reaction velocity remains to be explained. It will be seen from the table that whereas, at lower temperatures, the temperature coefficient is small, it rapidly increases above about 20°. This type of relation

makes inapplicable of course the ordinary kinetic interpretation of the temperature coefficients of thermal reactions based on the Arrhenius equation for the temperature coefficients

$$\frac{d\ ln\ k}{dT} = \frac{A}{T^2}$$

which assumes only molecules possessing the "activation" energy $\frac{A}{R}$ to be capable of reaction and attributes the accelerating action of temperature mainly to an increase in concentration of these energy-rich molecules. Further, the dependence of the isomerisation and bromination rates on the temperature is not the same. To account for this last effect, Wachholtz assumes that the life of the intermediary compound (the "quasi-molecule") changes with temperature and thus changes the probability of its collision with a bromine molecule. The general shape of the temperature function of both the isomerisation and the bromination reaction rates requires another assumption, namely, that the relative probability that the intermediary compound be decomposed or transformed into the radical, changes with temperature. Wachholtz suggests that, at about 20°, a new degree of intramolecular freedom in ester molecules comes into play and changes the stability of the "quasi molecule." Altogether, the theory put forward by Wachholtz gives a sufficiently complete account of all properties of the reactions studied, although, as seen, several assumptions not otherwise supported must be introduced. There is, on the other hand, no evidence against the possibility of those properties of the intermediary products which have been assumed by Wachholtz and probably only further experiments can decide the question of their existence or not.

Isomerisation of Benzoylacrylic Acid Derivatives. Rice [62] has found that benzene solutions of the yellow methyl and ethyl esters of benzoylacrylic and of para-methoxy-benzoylacrylic acids are transformed in sunlight into unstable colourless isomers. In the presence of small quantities of bromine and of iodine, however, the reverse reaction takes place in sunlight. This is a case of pure photosensitisation, since the halogens themselves do not undergo any chemical change. It promises some interesting points for a future investigation, but at present no kinetic data are available to warrant further discussion.

Sensitisation by Uranyl Salts. Already in the beginning of the nineteenth century it was discovered that, in presence of uranyl

[62] *J. Am. Chem. Soc.*, **45**, 222 (1923); **46**, 214 (1924).

salts, certain reactions were accelerated by sunlight. Since then the photosensitising action of uranyl salts has been the object of a large number of investigations and it has been found that the number of photochemical reactions which can be realised by addition of uranyl salts is extraordinarily large. For the most part, the observations made have been of a qualitative character or the investigators have studied the preparative side of the reactions, so that, at present, kinetic data are available for only a few reactions of this type.

Before the discussion of these kinetic data, it is worth while to remark that the expression "photosensitisation" is not strictly valid for some uranyl salt reactions, since, in these, the uranyl ion is simultaneously reduced to the uranous state ($U^{\cdots}$). However, we shall see that the kinetics of these reactions are similar to the purely sensitised processes and their treatment here appears desirable.

Sensitised Decomposition of Oxalic Acid. A reaction which offers the least difficulties in the interpretation of the experimental results and which has been the object of a most extensive study, is the decomposition of oxalic acid in presence of uranyl salts. Of the more recent investigations may be mentioned that of Fay,[63] who found that, besides carbon dioxide, carbon monoxide and formic acids are formed in this reaction and that the uranyl group is partly reduced to uranous ion. Berthelot and Gaudechon[64] state that no formic acid is formed, but Bruner and Kosak[65] find this acid among the decomposition products. Bacon[66] studied more extensively the kinetics of this reaction in sunlight. He found the violet and ultraviolet part of the spectrum to be effective and observed that the rate of oxalic acid decomposition was completely independent of the acid concentration. Furthermore, the rate of reaction was not measurably affected by a temperature change from 20° to 100° and by addition of different acids and bases, so long as the solution remained acid. In neutral solutions the reaction is complicated, as Fay already observed, by the formation of a precipitate, containing uranium oxides. Bacon further found that the rate of reaction increased with increasing uranyl salt concentration, and remained constant if, instead of uranyl sulfate, an equimolecular amount of uranyl nitrate was added to the oxalic acid.

Boll[67] obtained different results, working with very dilute solutions of uranyl acetate (0.001 *N*) in ultraviolet light of the wave

[63] *J. Am. Chem. Soc.*, **18**, 269 (1896).
[64] *Compt. rend.*, **157**, 333 (1913); **158**, 1791 (1914).
[65] *Z. Elektrochem.*, **17**, 354 (1911).
[66] *Filippine J. Sci.*, **2**, 129 (1907); **5**, 281 (1910).
[67] *Compt. rend.*, **156**, 1891 (1913).

length 2500 Å. Boll observed that the rate of reaction was approximately proportional to the oxalic acid concentration and that, further, about 50 molecules reacted per absorbed quantum.

Recently, Anderson and Robinson,[68] working with more concentrated solutions of acetic acid and uranyl salts, determined the yield as about 0.03, but this value, as also that of Boll, seems to be incorrect, since Bowen and Watts [69] found that one molecule of oxalic acid is decomposed per absorbed quantum, in good agreement with earlier determinations of Büchi [70] for the quantum yield of visible light. Although no definitive explanation of the possible errors in the experiments of Boll and of Anderson and Robinson can be given at present, their large deviation and the agreement of Büchi's and Bowen and Watts' results are decisively favourable to the conclusion that, in this reaction, the quantum yield is close to unity.

Büchi carried out a careful investigation of the reaction kinetics. His results are in very good agreement with experiments of Bacon, but some interesting new effects were also observed. The rate of reaction was found to be independent of the oxalic acid concentration only so long as this was in excess of uranyl sulfate. For lower relative concentrations of oxalic acid a decrease in the rate of reaction was observed. In Table 22, which represents his results, x indicates the ratio of oxalic acid to uranyl sulfate concentrations.

TABLE 22.

x	∞	2	1.5	1.0	0.5	0.25
Relative rate	1.00	0.940	0.915	0.785	0.452	0.252
Calcul. I	1.00	1.00	1.00	1.00	0.500	0.250
Calcul. II	0.915	0.736	0.672	0.575	0.405	(0.252)

It was also found that addition of sulfuric acid ($5H_2SO_4$ to $1H_2C_2O_4$) decreased the rate of reaction by 34 per cent, when 0.033 N oxalic acid and 0.0166 N uranyl sulfate were used. Addition of hydrochloric (0.0666 N) or formic acids (0.0666 N) hardly affected the rate of reaction. Büchi studied also the reaction products. He found that formic acid was formed up to 40 per cent of decomposed oxalic acid and that the yield of formic acid decreased in more acid solutions. The yield of uranous salt increased in acid solutions up to about 3 per cent of the equivalent of decomposed oxalic acid. Discussing the possible explanation of these observations and of the quantum yield of unity, he suggested that, in solutions of uranyl salts containing

[68] *J. Am. Chem. Soc.*, 47, 718 (1925).
[69] *J. Chem. Soc.*, 127, 1607 (1925).
[70] *Z. physik. Chem.*, 111, 269 (1924).

an excess of oxalic acid, practically the total amount of uranyl ion is present in the form of a complex ($UO_2C_2O_4H_2$) and that this is the photosensitive component, which decomposes on absorption of an energy quantum either by the reaction:

$$C_2O_4H_2 \rightarrow CO_2 + CO + H_2O$$

or by the reaction

$$C_2O_4H_2 \rightarrow HCOOH + CO_2.$$

The reduction of uranyl ion is probably due to a secondary reaction, possibly with the formic acid formed.

The observations of Henri and Landau [71] on the absorption spectra in ultraviolet support this view. It was found that a marked increase in absorption of light (3200-2700 Å.) by uranyl salts is caused by addition of oxalic acid, although this latter alone shows only a weak absorption. The deviations from Beer's law indicate the formation of an UO_2—$C_2O_4H_2$ compound, even in the presence of strong acids.

Büchi suggested that, if the oxalic acid is present in less than equivalent amount, part of the light energy which is absorbed by the free uranyl ion (or the undissociated uranyl sulfate) is lost for the photochemical reaction. Let us assume for the moment that, if the uranyl sulfate is in excess, all the oxalic acid is present in the complex; then the relative rate of reaction will be given by the equation:

$$1. \quad \frac{\alpha_1 . x}{\alpha_1 x + \alpha_2(1-x)}$$

where α_1 and α_2 are the light absorption coefficients and x has the same meaning as in Table 22. If it be assumed further that α_1 and α_2 are equal, then we obtain values for the rate of reaction which are given in the table under "Calcul. I". Of course, this calculation is only a first approximation, since the decrease of the reaction velocity on addition of sulfuric acid indicates that the formation of the complex $UO_2C_2O_4H_2$ is not complete, but that an equilibrium exists between the uranyl sulfate molecules, uranyl ion, and uranyl oxalate. A corresponding correction in the equation for the relative reaction rate would tend to bring the calculated values closer to the observed ones. It would in general be possible to explain the decrease in the rate of reaction by the assumption that free uranyl ions absorb light and then either decompose oxalic acid on collisions or emit the light energy as fluorescence. This theory leads to an equation for the rate of reaction, which has already been derived in this book:

$$2. \text{ The relative rate of reaction} = \frac{x}{k + x}$$

[71] *Compt. rend.*, **158**, 181 (1913).

Values calculated with $K = 0.736$ are given in Table 22 under "Calcul. II" and indicate that this equation does not represent the experimental results.

Lactic Acid Decomposition. Bolin [72] observed very similar kinetic relations in studying the decomposition of lactic acid in presence of uranyl salts. The rate of reaction is again independent of the acid concentration so long as this is in excess and the process has a temperature coefficient 1.0 from 20° to 30°. With increasing uranyl salt concentration, the rate of reaction reaches a steady value, indicating a proportionality to the amount of absorbed light energy. The difference between the oxalic acid and lactic acids decompositions is that, whereas Büchi finds, in absence of oxygen, only a small yield of uranous salt (not over 3 per cent), Bolin finds under these conditions that an equivalent amount of uranyl ion is reduced to the tetravalent uranous ion. At the same time, he observes a decrease in the rate of reaction with time of illumination. Bolin suggests that the primary reaction is

$$CH_3CHOHCO_2H + UO_2^{\cdot\cdot} + 2H^{\cdot} \rightarrow CH_3CHO + CO_2 + 2H_2O + U^{\cdot\cdot\cdot\cdot}$$

and that, in presence of air or oxygen, the uranous ion is secondarily oxidised back to $UO_2^{\cdot\cdot}$.

Aloy and Rodier [73] find that, under the influence of light, the solutions of uranyl salts UO_2R_2 (R is a monobasic acid) undergo quite generally the reaction:

$$UO_2R_2 + 2RH + A \rightarrow UR_4 + H_2O + AO.$$

(A indicates an oxygen acceptor, for instance, ethyl alcohol which is oxidised to acetaldehyde.)

Formic Acid Decomposition. Less simple kinetic relations were found by Hatt [74] in the decomposition of uranyl formate. In this reaction, the uranyl ion is reduced to uranous ion and this latter shows a retarding effect on the rate of reaction, which is attributed by Hatt to the absorption of active light by it. Hatt further finds that the initial rate of reaction is proportional to the light intensity, which was varied in the ratio 1:280, and estimates the quantum yield to be about 0.4.

Büchi [75] compared the rate of decomposition of formic acid with that of oxalic acid and came to the conclusion that the quantum yield of the former reaction is about 0.7. Baur [76] pointed out that, in the

[72] *Z. physik. Chem.*, **87**, 490 (1914).
[73] *Bull. Soc. Chim.*, **31**, 246 (1922).
[74] *Z. physik. Chem.*, **92**, 513 (1918).
[75] *Loc. cit.*
[76] *Z. physik. Chem.*, **111**, 315 (1924).

initial stages of this reaction, the quantum yield is probably even larger than 0.7 and reaches unity. The decomposition of uranyl formate was found by Hatt to be very sensitive to addition of salts and acids, all of which cause a decrease of the reaction rate. Later, in connection with researches of Berger, who also studied the inhibitive effects in the formate decomposition, we shall have occasion to discuss these phenomena and shall now mention only the effects caused by vanadium salts. Hatt found that, on addition of pentavalent vanadium ions, the decomposition of uranyl-formate changed its character. Instead of uranyl ion reduction, the vanadium ions were reduced (to V^{IV}) and only after all pentavalent vanadium was consumed did the reduction of uranyl ions start. The presence of tetravalent vanadium also influenced the course of reaction since, when only these ions were added, the reaction showed a long induction period on illumination with practically no decomposition of formate during this time.

Besides these reactions, which are accompanied by a simultaneous reduction of uranyl ion, there are several processes known in which uranyl salts play only the rôle of photosensitisers. Plotnikoff [77] states that the polymerisation of vinyl chloride which proceeds under the action of extreme ultraviolet can be photosensitised by uranyl salts to visible light. Baur [78] describes some experiments with uranyl sulfate and mercuric chloride. In solutions of these substances no reaction is observed on illumination, but if sugar has been added and the system afterwards illuminated, then mercurous chloride is formed. Uranyl sulfate remains, according to Baur, unchanged.

Baur [79] developed, in a series of publications, a theory of light action on uranyl salts. In the later modification of his theory, Baur assumes that the action of light is comparable with electrolysis. On absorption of an energy quantum, the electronic orbits of an uranyl ion are distorted, with the result that one "end" of the molecule forms a cathode, the other an anode. This intramolecular electrolysis explains, in the opinion of Baur, the simultaneous reducing and oxidising action of illuminated uranyl salts on different substances. He considers the experiments with mercuric chloride and sugar as direct confirmation of his theory and ascribes to sugar the rôle of a cathodic depolariser necessary for the reduction of the mercuric chloride. Baur further suggests that even the photosensitising action of certain dye-

[77] *Z. wiss. Phot.*, 21, 117 (1922).
[78] *Helv. chim. Acta* 1, 186 (1918).
[79] *Loc. cit.*, also *Schweiz. Chem. Zeit.*, 2, 40 (1918); *Z. Elektrochem.*, 25, 102 (1918); 27, 72 (1921).

stuffs is caused by a similar primary formation of a molecular cathode and anode.

Sensitisation by Dyestuffs. Important experiments on the photosensitising action of dyestuffs have been described by Gros,[80] who studied the oxidation of colourless leuco bases of some derivatives of fluorescein in aqueous solutions. He observed that the rate of oxidation, which showed a marked autocatalytic effect if a pure leuco base was originally used, could be increased manyfold by addition of some other dyestuff of the same group. He demonstrated further that this action was due to absorption of light by the dyestuff added. From the data contained in Gros' paper we can see that every dyestuff acts as a photosensitising agent on the oxidation of leuco bases under the influence of only those wave lengths which are absorbed by it. For instance, the photosensitising action of tetrachloro-tetrabromo-fluorescein is reduced relatively less by a light filter containing bichromate solution, than is the action of non-substituted fluorescein, since the former substance has an absorption band which extends to longer wave lengths (transmitted by the bichromate) than the absorption band of fluorescein. Gros further observed that, by increasing the concentration of a photosensitising dyestuff, a maximum of the reaction velocity could be obtained and that further increase of dyestuff concentration retarded the rate of reaction. As an example, the data on the action of tetrachlorotetrabromofluorescein on the oxidation of fluorescein leuco base are represented in Table 23.

TABLE 23.

Concentration of the photosensitiser	0.0	0.0004	0.001	0.002	0.004 molal
Relative rate of reaction	14.0	102.6	101.6	89.6	73.1

A relevant explanation of this effect is that, in concentrated solutions of the dyestuff, light is absorbed in the first thin layer of the solution and the rate of reaction is determined in this case mostly by the slow rate of diffusion of oxygen and leuco base to the illuminated layer. Confirming this suggestion is Gros' observation that the deeper coloured poly-substituted fluorescein dyestuffs show decrease in the rate of reaction in more dilute solutions than the lighter coloured ones.

The experiments of Gros demonstrated that the oxidation of leuco bases to dyes is photosensitised by several dyestuffs and that this effect is due to absorption of light by them. The inner mechanism of the reaction remains, however, unknown. Whether a dyestuff mole-

[80] *Z. physik. Chem.*, 37, 122 (1901).

cule activates, on light absorption, a leuco base molecule or oxygen, or whether initially, a complex of a leuco base and a dyestuff molecule is formed and this is the photosensitive component, cannot be deduced from Gros' experiments.

Tappeiner and Jodlblauer [81] demonstrated that, by means of different dyestuffs, many inorganic and organic reactions can be photosensitised to visible light. The subject was followed by Winther and by others. We shall have the opportunity to discuss some of these reactions in the next chapter. From the biological point of view the experiments of Neuberg [82] and his co-workers on photochemical reactions of organic matter, photosensitised by dyestuffs and different inorganic substances are interesting.

Sensitisation of Photographic Emulsions. As a result of a long series of technical and scientific investigations, following the discovery of Vogel, earlier mentioned, different dyestuffs have been found by means of which photographic plates can be sensitised now to all parts of the visible spectrum and even to the shorter intra-red. Simultaneously, certain general rules determining the usefulness of different dyestuffs as photosensitisers of photographic process have been advanced.

It was found that only dyestuffs adsorbed by the silver halide particles can act as photosensitising agents and that those substances which are themselves sensitive to light show a more pronounced action. On the other hand, marked fluorescence of the dyestuffs decreases their usefulness as photosensitisers. On the whole, although much has been written on the subject of photosensitisation of photographic emulsions by dyestuffs, even now the mechanism of this process is not definitively elucidated. Possibly some indications as to the mechanism of this action will be obtained from a comparison with the effects of silver bromide photosensitisation by adsorbed ions. It was well known that silver halides precipitated in excess of soluble silver salts possessed a higher sensitivity to illumination, than those precipitated in excess of a halide ion. The usual interpretation of the effect was that silver ions present in the emulsion play the rôle of halogen acceptors and prevent the recombination of silver and halogen atoms formed upon illumination.[83]

Fajans and Frankenburger [84] studied the spectral sensitivity of

[81] *Ber.*, 38, 2607 (1905).
[82] *Biochem. Z.*, 13, 27, 29, 61.
[83] Comp. Plotnikoff, "Lehrbuch der Photochemie," 1921.
[84] *Z. Elektrochem.*, 28, 499 (1922).

variously prepared silver bromides. They found that silver bromide prepared by the action of bromide on solid silver and then degassed in vacuum, and thus free from any adsorbed substances, is sensitive only to light of shorter wave length than about 4350 Å. The same spectral sensitivity was also shown by silver bromide precipitated in excess of bromide ions and illuminated afterwards in presence of acid bromine acceptors (H_2SO_3). On the other hand, silver bromide, which was precipitated in excess of silver nitrate, was found to be sensitive to the whole visible spectrum, including the wave lengths longer than 6200 Å. The same spectral sensitivity was observed with silver bromide prepared in an excess of bromide ions but illuminated in presence of basic bromine acceptors (KOH, etc.). Fajans and Frankenburger could further demonstrate that even red light caused the decomposition of silver bromide (and not some other reaction), since products of the interaction of bromine with acceptors could be identified after an illumination.

It is characteristic of the action of red light that it causes only the decomposition of the surface layer of silver bromide and that this latter is sensitive afterwards only to light of wave length shorter than about 5780 Å. Silver bromide prepared in vacuum and sensitive only to blue light can also be made sensitive to all wave lengths below 5780 Å., by an initial illumination with light of shorter wave length than 4350 Å.

The theory advanced by Fajans, which tries to explain uniformly all these observations, is based mainly on the following data earlier obtained. The x-ray spectrograms of precipitated silver halides have demonstrated their crystalline nature. On the other hand, it was known [85] that, depending on the mode of preparation, silver bromide particles are positively or negatively charged and that they contain a surface layer of adsorbed ions. Fajans interpreted these observations by suggesting that silver ions are adsorbed on the surface of silver bromide precipitated in excess of silver salt and cause its positive charge, whereas the (hydrated) nitrate ions, although attracted by the positive charge, remain at a larger distance from the surface. On the other hand, on silver bromide prepared in excess of bromine ions, these latter are mainly adsorbed and cause the negative charge of the surface. Fajans proposed the following diagrammatical representation of these effects;

[85] Lottermoser, *Z. physik. Chem.*, 60, 451 (1907); 62, 359 (1908); 70, 239 (1910); Fajans and Beckerath, *Z. physik. Chem.*, 97, 478 (1921).

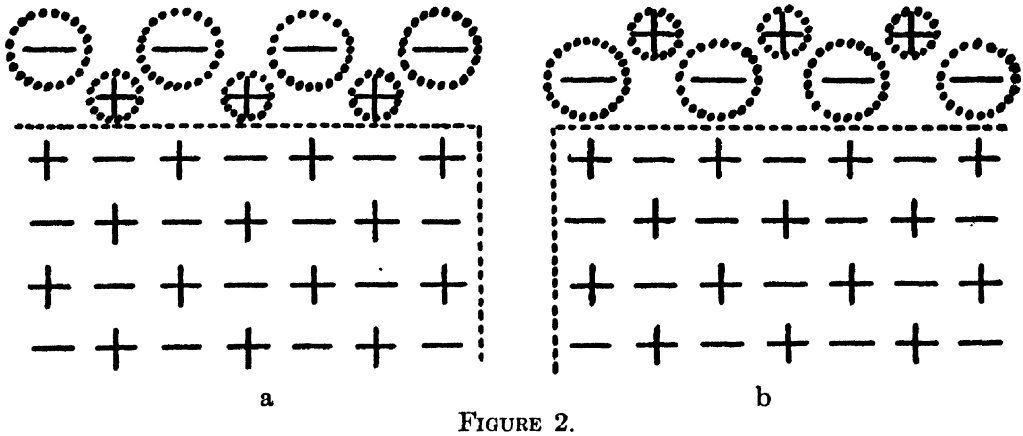


FIGURE 2.

The primary action of light on silver halides consists, in the opinion of Fajans, in the shift of the valence electron from a bromide to a silver ion and thus in the formation of two atoms.

As indicated by diagram *a*, the silver ions are close to the illuminated surface and, through their positive charge, reduce the minimum quantum energy necessary for this process. On the other hand it can be expected that, on surfaces represented by the second scheme, the same minimum energy is required for the shift of an electron, as is required on a clean silver bromide surface and this is confirmed by experiments of Frankenburger.

Fajans further suggested that the sensitivity of negatively charged silver halide surfaces in alkaline solutions to longer light waves is due to adsorption of hydroxyl ions. Supporting this idea is the observation of Frankenburger that silver hydroxide itself is sensitive to the whole visible spectrum, even to the red. Evidently less energy is required for the shift of an electron from hydroxyl than from bromide to silver ions. The temporary character of the sensitivity to red light is due to removal of the adsorption layer and to the formation of a layer of silver atoms. It now remains to be explained why sensitivity to light below 5780 Å. is set up, and not to light below 4350 Å., as is initially the case with clean surfaces of silver bromide. Fajans pointed out that, since the energy of dissociation of solid silver bromide into free atoms is about 111,000 cal. per gram mol., and since the non-photosensitised decomposition can be caused already by light of wave length 4350 Å., which corresponds to only 65,000 cal. of quantum energy, the products of the primary photochemical process must be adsorbed and not free atoms (at least that of silver).

The energy required for this process will be 111,000—x cal. and, since x—the heat of adsorption of silver atoms—can amount to more

than 30,000 cal., it is prorbable that 65,000 cal. of the radiation energy will be sufficient to cause the decomposition into bromine and adsorbed silver atoms. Fajans further suggested that the sensitivity of silver bromide to all light of shorter wave length than 5760 Å., setting in after an initial illumination, must be attributed to the formation of an adsorption complex: Ag-BrAg in which the dissociation energy is further lowered by the simultaneous action of adsorbed silver atoms.

Recently, Masaki [86] claimed that a heating of photographic plates to about 100° photosensitises them to extremely long light waves. In this way Masaki photographed, with ordinary plates, spectra up to 8000 Å., and, by means of panchromatic plates, even up to 10,000 Å. The nature of this heat photosensitisation has not been studied, but since silver halides in absence of gelatin do not show a similar effect, it is probably due to some chemical process, during the heat treatment, in which gelatin takes part.

Different in nature from the above discussed processes is the photosensitisation of ordinary photographic plates to extreme ultraviolet. We have noted, in an earlier chapter, that gelatin shows an increasing absorption with decreasing wave length. Light below approximately 2000 Å. is actually so strongly absorbed by gelatin that practically no light energy can reach the silver halide particles and be utilised for the photochemical process. Coating of photographic emulsions with certain substances (mineral oils), which, under the action of short ultraviolet light, emit fluorescent light of longer wave length, is the method frequently employed to obtain photographs of the short ultraviolet spectral region. The emitted fluorescence must, of course, belong to a spectral region which causes the decomposition of silver halides, but is less strongly absorbed by gelatin.

Sensitisation by Zinc Oxide. A large variety of photosensitised reactions has been shown in recent years to be due to the action of solid particles of zinc oxide. Eibner [87] demonstrated that oil paints containing zinc oxide are more rapidly destroyed by light than those containing other inorganic substances.

Winther [88] studied the fluorescence of zinc oxide and some of its photosensitising actions. For both processes, the near ultraviolet spectral region was found to be effective. Winther demonstrated that, in presence of illuminated zinc oxide, glycerin is oxidised to glycerose and that this process can be carried out either in presence of free oxygen or in presence of different inorganic compounds. In absence

[86] *Japan J. Phys.*, **2**, 163 (1923).
[87] *Chem. Z.*, **35**, 753 (1911).
[88] *Z. wiss. Phot.*, **21**; **45**, 141, 168, 175 (1921).

of air, lead carbonate is, for instance, reduced to metallic lead by the reducing action of glycerin. Winther suggested that the zinc oxide remains chemically unchanged during these reactions and supported his view by experiments, which indicate that actually the size and shape of single zinc oxide particles remain unchanged even on prolonged illumination in presence of glycerin and lead carbonate. Further, some other oxidations (of dyestuffs) in presence of zinc oxide were observed by Winther.

Winther also claimed that ozone is produced when zinc oxide is illuminated in presence of oxygen. This photosensitised formation of ozone is due to light of even smaller quantum energy than in the reaction of excited mercury atoms studied by Dickinson and Sherrill.[89] However, the only test of ozone formation in Winther's experiments was the oxidation of potassium iodide and it is questionable whether hydrogen peroxide may not result from the action of illuminated zinc oxide on water and oxygen. The research of Winther is not decisive but it shows that some volatile peroxide must have been formed on illumination of zinc oxide. A theory, which was advanced by Winther and which was considered by him to account not only for the photosensitisations by zinc oxide, but also for some other reactions, implies that the photosensitisers emit the absorbed light as fluorescence. This secondary radiation is supposed to be of much shorter wave length than the absorbed light, and be thus strongly absorbed by oxygen and other substances. Winther observed that no ozone could be obtained when zinc oxide was illuminated in an evacuated vessel provided with a fluorite or quartz window and concluded that the emitted radiation is below 1800 Å. This theory is in direct disagreement with Stokes' Rule concerning fluorescence and with the general concepts of the transformations of radiation energy according to quantum rules.

Tammann[90] observed that, in presence of solid zinc oxide, silver is deposited from a solution of silver nitrate on illumination and zinc goes into solution. Tammann suggested that light accelerates the ionic exchange according to the equation:

$$ZnO + 2AgNO_3 \rightarrow Ag_2O + Zn(NO_3)_2$$

Kohlshütter and d'Almendra[91] demonstrated, however, that metallic silver and not its oxide is the product of light action. Further and more quantitative investigations of this reaction have been carried

[89] *Loc. cit.*, p. 131.
[90] *Z. anorg. Chem.*, 114, 151 (1920).
[91] *Ber.*, 54, 1961 (1921).

out by Baur and Perret [92] and by Perret [93] himself. The experimental method consisted in exposing to sunlight a suspension of zinc oxide or other insoluble inorganic substances in silver nitrate solutions. The results indicate that the photosensitised decomposition of silver nitrate solution is due to a specific action of zinc oxide and not to the presence in general of solid particles in the solution. It was further observed that, on short illumination, not only metallic silver, but also silver oxide and peroxide are deposited on zinc oxide surfaces and that an equivalent amount of this latter goes into solution. On longer illumination, the amount of silver peroxide decreases, probably on account of secondary decomposition in presence of illuminated zinc oxide. The photochemical reaction was also found to be followed by evolution of gas, identified as pure oxygen. Perret suggested that the integral process taking place on illumination is expressed by the following stoichiometric equation:

$$2AgNO_3 + ZnO\ (+ \text{light}) \rightarrow 2Ag + Zn(NO_3)_2 + 1/2O_2$$

and demonstrated that, actually, the total amount of oxygen formed (free and bound in silver oxides) is given roughly by the relation

$$1/4\ O_2 = Ag.$$

He further applied the theory of Baur, mentioned earlier, to the reaction and suggested that the absorption of light by zinc oxide results in an "intramolecular electrolysis" and in the formation of molecular cathode and anode. The observed reaction is due to secondary ionic processes according to the schemes:

$$\text{I} \quad ZnO \begin{cases} {}^{+} + OH^- \rightarrow 1/4O_2 + 1/2H_2O \\ {}^{-} + Ag^+ \rightarrow Ag \end{cases}$$

$$\text{II} \quad ZnO \begin{cases} {}^{+} + OH^- \rightarrow \text{silver peroxide} + 1/2H_2O \\ {}^{-} + Ag^+ \rightarrow Ag \end{cases}$$

Silver ions are supposed to play the rôle of cathodic depolarisers and the process is, according to Baur, a hidden electrolysis of water.

Perret observed that solid particles of zinc oxide exert a specific photosensitising action also on solutions of mercuric chloride. In this process, as in that with silver nitrate, zinc goes into solution in amount equivalent to reduced mercury salt. The results of Perret's measurements are expressed by him by means of the following stoichiometric equation:

$$2HgCl_2 + ZnO\ (+ \text{light}) \rightarrow Hg_2Cl_2 + ZnCl_2 + 1/2O_2.$$

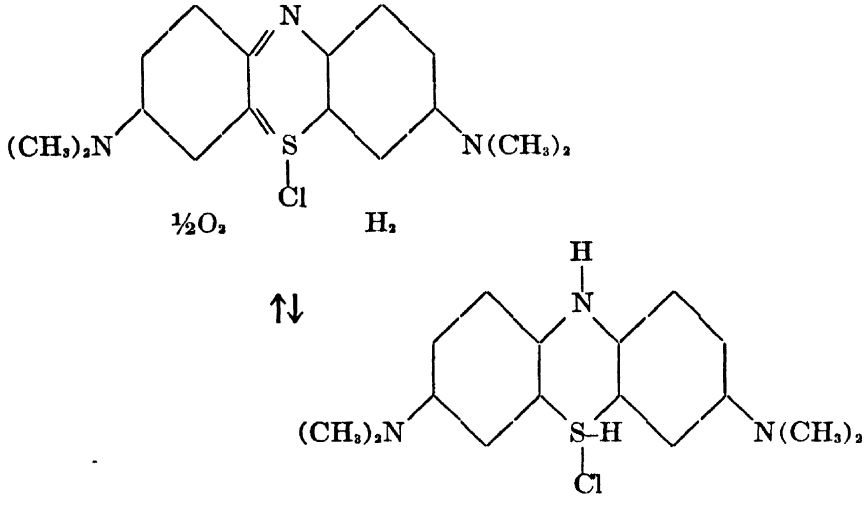
Presence of glucose in solution not only notably increases the rate of photochemical reduction, but also changes its course, since Perret

[92] *Helv. chim. Acta.*, 7, 910 (1924).
[93] *J. Phys. Chem.*, 23, 97 (1926).

observed, in this case, a formation of metallic mercury. In presence of glucose, the rate of reduction of mercuric chloride in light is approximately independent of its concentration. According to Baur's theory, the reduction of mercuric chloride by illuminated zinc oxide will be represented by the following scheme:

$$ZnO \begin{cases} {}^{+}+OH^{-} \rightarrow 1/4O_2 + 1/2H_2O \\ {}^{-}+HgCl_2 \rightarrow 1/2Hg_2Cl_2 + Cl^{-} \end{cases}$$

The third reaction of zinc oxide, studied by Perret, was its action in light on methylene blue. Methylene blue has been known for a long time to be sensitive to light. Lasareff [94] studied the kinetics of reduction of methylene blue solutions in solidified gelatin. He found that the process was reversible and that, under the influence of free oxygen, the methylene blue leuco base was oxidised in the dark to the dyestuff again:



Chakravarti and Dhar [95] have demonstrated recently that methylene blue undergoes, on illumination, besides this reversible reduction, an oxidation process, if oxygen is present in the solution. According to Perret,[96] the photochemical reaction of methylene blue is noticeably accelerated by the presence of zinc oxide. The bulk of the methylene blue is reduced to leuco base and can be recovered again if the solution is left for a time in contact with oxygen. Perret's colorimetric observations demonstrated, however, that the process was not completely reversible and Perret suggested that a part of the methylene blue is oxidised in presence of zinc oxide, even in solutions illuminated in absence of oxygen. Perret further found that this oxidation, which

[94] *Z. physik. Chem.*, 78, 661 (1912).
[95] *Z. anorg. Chem.*, 142, 299 (1925).
[96] *Loc. cit.*

amounted to about 20 per cent of the reacting mass, was reduced to only about 7 per cent by addition of glucose. The fate of the zinc oxide in this photosensitised reaction was not investigated. Presumably it remains unchanged. Baur's theory describes the reaction by the usual scheme involving a "hidden" electrolysis of water:

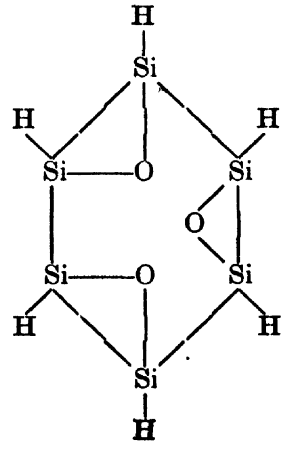
$$ZnO\begin{cases}^{+}+OH^{-} \rightarrow \text{oxidation product} + 1/2H_2O \\ ^{-} + \text{methylene blue} \rightarrow \text{leuco base}\end{cases}$$

In a formal way these schemes, of course, account for the simultaneous oxidations and reductions which we have met on preceding pages and earlier in this book. On the other hand, the ratio of oxidised and reduced substance is never stoichiometric, so that Baur is forced to introduce secondary reactions "at the electrodes." On account of this, the theory loses its simplicity and much of its power to predict the course of events.

The effect of "cathodic depolarisers" is as easily explained on the basis of primary formation of excited molecules and their secondary reaction with reducing substances.

The study of the kinetics of such reactions as those of zinc oxide meets large difficulties, mainly on account of the heterogeneity of the reacting substances. Even more difficulties will be encountered in their quantitative treatment on the basis of the equivalence law. In the meantime, Baur's theory offers a convenient, if only a formal way of describing them.

Sensitised Reactions of Siloxene. Particularly interesting for the general theory of photosensitisation are the experiments of Kautsky on the reactions of siloxene and its substitution and oxidation products. Kautsky and his co-workers ascribe to siloxene, a crystalline colourless substance, extremely reactive and a strong adsorbent, the following ring structure:



This substance can be easily oxidised or halogenated to the stable silicon dioxide or to the fully halogenated products, but, ordinarily, different intermediate compounds of varying composition can be obtained, compounds which are usually intensively coloured.

Kautsky and Thiele [97] observed that, whereas siloxene reacts rapidly with inorganic chlorine compounds, its reaction with chlorine substituted organic substances does not proceed in the dark under ordinary conditions at all. This last reaction, however, can be induced by illumination and if, initially, a pure colourless siloxene has been used, the rate of reaction shows a marked autocatalytic effect.

Kautsky and Thiele demonstrated that the autocatalysis is due to intermediary formation of coloured halogenation products, which photosensitise the original reaction of siloxene to visible light. A similar photosensitisation to visible light can be obtained by means of, for instance, rhodamine, but the necessary condition is that the dyestuff be adsorbed on siloxene.

Kautsky and Thiele suggest that, in these processes, only those molecules can transmit the absorbed light energy to siloxene and thus activate it for a reaction, which are in close proximity to siloxene crystals. They further demonstrate that the activation energy, necessary for certain reactions of siloxene, can be obtained from a simultaneously proceeding exothermic reaction of the siloxene.

Chemiluminescence as Reversed Photosensitisation. The effects of photosensitisation of siloxene by dyestuffs are particularly interesting because they are to a certain extent reversible. Kautsky and co-workers [98] demonstrated that siloxene can be brought to chemiluminescence by a rapidly proceeding exothermic reaction, for instance, oxidation by permanganate. If some dyestuff (rhodamine) be adsorbed on siloxene and this latter subsequently oxidised, then light is emitted also by the dyestuff molecules. Kautsky showed that the spectral distribution of this induced chemiluminescent light is identical with the distribution of the usual fluorescence of the same dyestuff and that, further, the emission of light is not due to a partial oxidation of the dyestuff by permanganate but to the reaction of siloxene. It must be concluded that the reaction energy is transmitted from the reaction products to dyestuff molecules and that the resulting excitation is identical with that produced in the dyestuff by absorption of radiation energy. This induced chemiluminescence cannot be due to a primary emission of light by reacting siloxene molecules and its subse-

[97] *Z. anorg. Chem.*, **144**, 197 (1925).
[98] *Z. Elektrochem.*, **29**, 308 (1923); *Z. Physik*, **31**, 60 (1923).

quent absorption by dyestuff since Kautsky demonstrated that the latter had to be adsorbed on siloxene in order to show the effect. The energy must evidently be transmitted by some sort of molecular "collision" between the adsorbed dyestuff and the neighbouring reacting siloxene molecules and the whole process is a direct reversal of the photosensitisation of siloxene already described.

These conclusions of Kautsky are corroborated to a certain extent by other studies on the effects of chemiluminescence, which reveal that, generally, the mechanism of induced chemiluminescence can be regarded as complementary in nature to the mechanism of photosensitisation.

Chemiluminescence by Combination of Atomic Hydrogen. Bonhoeffer,[99] for instance, observed that, when hydrogen atoms recombine in presence of alkali metal vapours or anthracene, a chemiluminescence is excited and the emitted spectrum is identical with the line spectra of the metal vapours or with the ordinary fluorescence spectrum of anthracene. Only those lines were observed by Bonhoeffer, of which the quantum energy is less than the heat of recombination of hydrogen atoms. An exception to this rule is Bonhoeffer's observation that the mercury line 2536 Å. is emitted when liquid mercury is present in the system. Bonhoeffer's idea as to the mechanism of these effects is that the recombination of hydrogen atoms takes place in a trimolecular process and the energy set free by the formation of the hydrogen molecule is transmitted to the third body, mainly in the form of intramolecular excitation energy.

Such an explanation of the emission of the mercury resonance line meets some difficulties, since the excitation of mercury (112,000 cal.) requires more energy than can be supplied by the recombination of hydrogen atoms (101,000 cal.). Bonhoeffer pointed out, however, that the mercury line is always accompanied by the emission of certain bands, which are known to belong to mercury hydride HgH,[100] and concluded that the mechanism of excitation of mercury atoms is probably not simple but involves several steps, in which the necessary quantum energy is gradually accumulated. Other effects of induced chemiluminescence, which involve the collisions of newly formed molecules possessing a large excess of energy, were initially discovered by Haber and Zisch,[101] who observed that reactions of vapourised metals with halogens were accompanied by emission of light. With alkali vapours the light consisted mainly of the resonance lines—the D-lines

[99] *Z. physik. Chem.*, **116**, 394 (1925).
[100] Compton and Turner, *Phil. Mag.* **48**, 360 (1924).
[101] *Z. Physik*, **9**, 302 (1922).

of sodium or corresponding lines of other alkali metals; with mercury, however, as the emitted spectrum did not contain the (resonance) line 2536 Å., the explanation suggested itself, that the heat of reaction of mercury with halogens is insufficient for excitation of mercury atoms.

Kallman and Franz [102] demonstrated, however, that the mercury line is emitted when a mixture of sodium and mercury reacts with chlorine (but not with bromine). The authors suggested that the reactions of metals with halogens proceeded in two steps:

$$1.\ Na + Cl_2 \rightarrow NaCl + Cl$$
$$2.\ Na + Cl \rightarrow NaCl.$$

The products of the second reaction possess a large surplus energy, which is equal to:

$$Na + Cl \rightarrow NaCl + 109{,}000 \text{ cal.}$$
$$Na + Br \rightarrow NaBr + 101{,}000 \text{ cal.}$$

Considering the possible uncertainties in these heats of reaction we see that, whereas an excitation of mercury atoms requiring 112,000 cal. can probably take place on collision with a newly formed NaCl molecule, this process must be considerably less probable when NaBr molecules or the still less energy-rich $HgCl_2$ molecules are formed.

Polanyi and Beutler [103] showed that, not only the reaction of sodium vapour with free halogens was accompanied by emission of the D-lines, but also its reaction with different halogen-containing inorganic substances. No emission of light could be observed with organic halogen compounds. Particularly interesting are the kinetic observations of Polanyi and Beutler. They indicate that the reaction of sodium and iodine actually proceeds in two steps and that, whereas the first step, which is unaccompanied by chemiluminescence, takes place on practically every collision of the reacting bodies, the second reaction is about 100 times slower (at a pressure of about 0.01 mm.), but is accompanied by emission of the line spectrum of the alkali metal.

Polanyi and Beutler accepted the reaction scheme postulated by Haber and Zisch and suggested that the second step, the reaction of the free atoms, is the slower process. They estimated, further, the intensity of the emitted light and came to the conclusion that about 10^{-4} of all collisions of sodium and iodine atoms are followed by the emission of light.

In order to follow Polanyi's discussion of the reaction kinetics we must return to the theory of Born and Franck [104] mentioned earlier.

[102] *Naturwiss.*, 13, 441 (1925).
[103] *Ibid.*, 13, 717 (1925).
[104] *Z. Physik*, 31, 411 (1925).

These authors pointed out that a molecule, formed as a result of collision of two atoms, will possess a surplus intramolecular energy equal to

$$Q + q = Q_1$$

where Q is the heat of reaction and q is the energy of the relative translational motion of atoms before the collision, according to the laws governing collision. Since a molecule can take up energy only in definite amounts, corresponding exactly to the energy differences of its different quantum levels, and since the probability that the total reaction energy Q_1 is equal to one of these energy levels is negligibly small, Born and Franck conclude that, in general, no reactions of this type can take place. They suggest, however, that the two atoms can form on collision a non-quantised "quasi-molecule," but unless some other body receives the surplus energy on collision, the quasi-molecule will be unavoidably decomposed again into atoms within a short time, the duration of which Born and Franck estimate to be about 10^{-13} seconds. In the opinion of Polanyi, the theory of Born and Franck is in serious disagreement with his own experimental results. If, actually, the secondary collision of a sodium atom, which leads to its excitation and to the formation of an NaCl molecule, follows the primary collision of a sodium and an iodine atom within the estimated short time interval of 10^{-13} seconds, then the rate of the reaction and the intensity of the resulting light emission should be, at the pressure of the experiments (0.01 mm. Hg), only 1×10^{-4} of the actually observed rate. Polanyi and Wigner [105] suggest accordingly that the life of the "quasi-molecules" is at least of the order of 10^{-9} seconds.

A different aspect of the whole process was put forward by Ljalikov and Terenin,[106] as the result of their spectroscopic observations on the reactions of different alkali metals with iodine. Ljalikov and Terenin point out that besides the reaction mechanism already mentioned:

$$\begin{aligned} \text{I.}\quad & M + I_2 \rightarrow MI + I + q_1 \\ & I + M \rightarrow MI + q_2 \end{aligned}$$

with the heats of reaction q_1 and q_2, the whole process could be imagined to take place in the following steps:

$$\begin{aligned} \text{II.}\quad & M + I_2 \rightarrow MI_2 + q_1' \\ & MI_2 + M \rightarrow 2MI + q_2' \end{aligned}$$

Ljalikov and Terenin suggest that the reactions of alkali metals with iodine proceed according to the second scheme and that the heat of

[105] *Z. Physik*, 33, 429 (1925).
[106] *Ibid.*, 40, 107 (1926).

reaction q_2' is divided equally between the two MI molecules formed. An approximate calculation of the heats of reactions shows, that $\frac{1}{2}q_2'$ is in all cases smaller than q_2 and thus makes possible an experimental test of both reaction schemes, since, according to the quantum theory, no line in the emission spectrum should be observed, the quantum energy of which ($Nh\nu$) is larger than the heat q of the reaction producing the energy. In the following table, Ljalikov and Terenin's results are represented, the observed lines being denoted by an asterisk.

TABLE 24.

Metal + I_2	q_1	q_2	$\frac{1}{2}q_2'$	Terms of the lines	Å.	$Nh\nu$ cal.
Li	64000 cal.	98000 cal.	81000	1S–2P	6708	42000 *
				1S–3P	3233	88000
Na	48000	82000	65000	1S–2P	5890.6	48000 *
				1S–3P	3302.3	86000
K	54000	88000	71000	1S–2P	7666	37000 *
				1S–3P	4044.8	70000 *
				1S–4P	3446.7	82000
Rb	54000	88000	71000	1S–2P	7800.9	37000 *
				1S–3P	4202.1	67000 *
				1S–4P	3349.5	85000

These experimental results certainly support the theory of Ljalikov and Terenin, since no line with higher quantum energy than $\frac{1}{2}q_2'$ has been observed.

Beutler, Bogdanyi and Polanyi [107] studied the reactions of sodium vapour with other halogens and observed in some cases in the emission spectra lines of even higher quantum energy than would correspond to q_2. Ljalikov and Terenin attribute this effect to an unequal distribution of the reaction energy q_2' between the molecules formed or to an intermediary formation of the compound M_2Cl_2 with double energy.

Their theory, however, meets certain difficulties in explaining the kinetic observations of Polanyi and Beutler [108] and besides, as the authors themselves pointed out, the emitted lines are broadened considerably more than would be expected on the basis of their theory. We shall not enter into further detailed discussion of these problems, since one point, which is of main importance to the theory of photosensitisation, seems to be well established by the experiments described. This is the experimentally tested suggestion that the excitation energy of a light emitting atom is transmitted to it on collision

[107] *Naturwiss.*, **14**, 164 (1926).
[108] *Loc. cit.*

the wave lengths emitted and the heat of the reaction is given by the quantum laws.

It is thus apparent that the process of induced chemiluminescence is the reversal of the phenomenon of photosensitisation. Of course, not all photosensitised reactions can be accounted for by a simple scheme involving only a transfer of energy on collisions of the primarily excited atoms or molecules of sensitiser with the reacting molecules. In certain cases an intermediary formation of molecular compounds or of adsorption complexes is undoubtedly in better agreement with the experimental data, but even in some of these reactions we can imagine the transfer of energy to occur via "intra compound" collisions of the sensitiser and reacting molecules. This suggestion, however, can hardly be applied to those cases where, as in photosensitisations by adsorbed ions, the absorption of light of a particular spectral region is caused only by formation of an (adsorption) complex and is probably due to a distortion of quantum levels in the reacting molecules by the sensitiser.

CHAPTER V

CATALYSIS AND INHIBITION

Sufficient experimental material has been presented so far to permit the conclusion that a vast majority of photochemical reactions can be influenced by substances which do not take part in the reaction. Substances absorbing light may act either as photosensitisers accelerating the rate, or as inner light filters retarding the rate of reaction by reducing the amount of light energy ordinarily available for the reaction. Of a different nature must be the effect of those catalysts and inhibitors which, although not absorbing light of the active wave lengths, nevertheless influence the rate of photochemical reactions.

It has been known already that numerous gaseous reactions require the presence of minute quantities of water vapour in order to proceed at measurable velocities. Unfortunately, the knowledge of this important phenomenon is limited practically to bare facts and its mechanism remains a complete mystery, except possibly in the case of the hydrogen-chlorine reaction. Not much more is known concerning the nature of the inhibiting action of oxygen, which is particularly pronounced in many reactions of the halogens. At one time, Bodenstein [1] even considered oxygen as a general cause of deviations of photochemical reactions from the equivalence law. Although his opinion was not confirmed by later investigations, it became evident that inhibition by oxygen is not restricted to the halogens alone, but is characteristic for several other photochemical reactions.

In the study of thermal reactions, various theories of catalytic and inhibitive mechanisms have occasionally been proposed and successfully applied to some particular class of reactions, although they seem to fail in other cases. A similar state of affairs will be found in the subsequent pages. It must be concluded that, just as the mechanism of different reactions is not the same, neither is the mode of action of catalysts or inhibitors. This latter action must similarly be a function of the nature of the reacting substances and therefore a single specified theory cannot account for all observations.

[1] *Z. physik. Chem.*, 85, 357 (1913).

Ozone Decomposition

In addition to the photochemical processes treated in previous sections, only one gaseous reaction—the decomposition of ozone—has been thoroughly studied with respect to the influence of catalysts. As a result of many different investigations it has been concluded that practically all gases influence, in some way, the rate of photochemical ozone decomposition. In order to simplify the discussion of the various observed effects we shall first consider only the action of those gases which remain themselves unchanged during the course of the reaction. In this case, the decomposition of ozone in light is stoichiometrically represented by the equation:

$$2O_3 \rightarrow 3O_2.$$

Regener [2] and later Weigert,[3] working with polychromatic ultraviolet light, found that the rate of this decomposition, per unit energy absorbed, increased with increasing concentration of ozone. Eva v. Bahr,[4] on the other hand, reported that the rate was proportional to the absorbed light energy, at least at very small partial concentrations of ozone. Oxygen was used as diluent in these experiments and Miss Bahr could observe that the rate of reaction was increased by a decrease of oxygen concentration. Warburg [5] studied the decomposition of ozone in monochromatic light (2530 Å.). He also measured the quantum yield and found it equal to 0.28 in mixtures of ozone and oxygen at atmospheric pressure. Ozone mixed with nitrogen or helium was found to decompose more rapidly, the quantum yield in nitrogen being equal to 1.1, in helium 1.7. These values were measured at atmospheric pressure in gases containing less than 0.7 per cent ozone. At higher partial pressures of the latter the quantum efficiency increased approximately as the square root of ozone concentration and became influenced by the intensity of incident light and the shape of the light beam. Moisture apparently decreased the rate of decomposition. Warburg pointed out that, since the wave length 2530 Å. is very strongly absorbed by ozone, the region where the photochemical reaction takes place at higher ozone concentrations, must be limited to a thin layer on the illuminated side of the vessel. Furthermore, since, under these conditions, the quantum yield is dependent on ozone concentration, it will be partly determined by the rate of ozone diffusion to the reaction zone. This effect will account

[2] *Ann. Physik*, 20, 1033 (1906).
[3] *Z. physik. Chem.*, 80, 78 (1912).
[4] *Ann. Physik*, 33, 589 (1910).
[5] *Sitzb. Preuss. Akad.*, 644 (1913).

for the influence of the light intensity and of the shape of the light beam, but of course will not explain Warburg's observation that only at low concentrations of ozone (below 0.7 per cent) the quantum yield remains constant.

Previously, the research of Ladenburg and Lehman [6] had demonstrated that ozone possesses a rather extended absorption spectrum. In addition to a strong continuous absorption below approximately 3000 Å., it has several absorption bands in the region 3000-3600 Å. and a group of bands in the visible part of the spectrum, particularly in the region 5000-6500 Å. In the infra red, according to Ladenburg and Lehman, ozone has an absorption maximum around 4.3 μ and also shows absorption of light of longer wave lengths. It was generally assumed that ozone was stable in visible light. Griffith and Shutt [7] demonstrated, however, that not only ultraviolet but also visible light absorbed by ozone accelerates the decomposition, although the resulting reaction is rather slow.

Griffith and McWillie [8] studied the kinetics of ozone decomposition in visible light. The rate of decomposition of ozone diluted by oxygen at atmospheric pressure proved to be proportional to $[O_3]^{3/2}$ over the concentration interval 10-1 per cent O_3. Since the absorption of light is incomplete at these low concentrations of ozone and therefore the amount of light energy absorbed is proportional to the ozone concentration, it is evident that, in visible light, an identical increase of quantum yield with ozone concentration, as in ultraviolet, takes place.

The Effect of Foreign Gases. Griffith and McWillie investigated extensively the effect of various gases on the rate of ozone decomposition. They confirmed the earlier observations of Warburg and found that, in composite mixtures at atmospheric pressure containing the same amounts of ozone, oxygen and one of the following gases, the rate of reaction increased in the order $O_2 \rightarrow CO_2 \rightarrow N_2 \rightarrow Ar \rightarrow He$. Previous to this, Stern and Volmer [9] in discussing Warburg's experiments had suggested that the primary action of light consisted in the formation of activated ozone molecules, and that these, before they had a chance to react, had lost part of their energy by collisions with oxygen molecules. In nitrogen and helium the yield of these inelastic collisions is smaller and therefore the rate of decomposition faster.

[6] *Ann. Physik*, 21, 305 (1906).
[7] *J. Chem. Soc.*, 119, 1948 (1921).
[8] *Ibid.*, 123, 2767 (1923).
[9] *Loc. cit.*, page

The same mechanism for the acceleration of ozone decomposition by different gases was advanced by Griffith and McWillie [10] and obtained later a quantitative confirmation in experiments by Kistiakowsky.[11]

Kistiakowsky studied the reaction in approximately monochromatic light, 6200 Å., and used, in contradistinction to other investigators, gas mixtures which contained up to 70 per cent ozone. The total pressure was varied from atmospheric to about 9 mm. The results of these experiments are rather complicated. At higher total pressure the rate of ozone decomposition is represented fairly well by the equation:

$$(1) \quad -\frac{d[O_3]}{dt} = k_1 I_{abs.} \frac{\sqrt{[O_3]}}{[O_2]}$$

At low pressures this equation does not satisfy the experimental results, the rate of reaction being only slightly retarded by oxygen and almost independent of ozone concentration. If the latter is kept constant, but increasing amounts of oxygen are added, the decrease of the reaction rate follows the equation which has already been derived for the extinction of gas fluorescence.[12]

$$(2) \quad -\frac{d[O_3]}{dt} = k_1 \frac{I_{abs.} k_2}{k_2 + k_3 [O_2]}$$

At higher oxygen concentration the rate of reaction is inversely proportional to it, as would be expected when, in Equation 2, k_2 becomes negligible in comparison with $k_3[O_2]$, as indicated by Equation 1. Experiments with gas mixtures containing various amounts of helium showed that the reaction rate may be represented by the equation

$$(3) \quad -\frac{d[O_3]}{dt} = k_1 I_{abs.} \frac{\sqrt{[O_3]}}{[O_2] + k'[He]}$$

The constant k' was found to be equal to 0.13, which means of course that helium retards the rate of reaction about 8 times less strongly than oxygen.

Examination of the data of the earlier investigations shows that they are, in general, consistent with the equations of Kistiakowsky. In particular it was found that the same value of k' (0.13) satisfies the experiments of Griffith. For Warburg's experiments in ultraviolet light, a slightly different value (0.16) must be used. The experiments of Griffith with gases other than helium are similarly well satisfied by Equation 3; but, of course, the values of k' are different, namely

[10] See also Griffith and McKeown, *Proc. Farad. Soc.*, **21**, 597 (1925).
[11] *Z. physik. Chem.*, **117**, 337 (1925).
[12] See page 128.

higher, which indicates stronger retarding action of these gases. All of this evidence strongly supports the theory of inelastic collisions of activated ozone molecules, accompanied by degradation of activation energy, as an important part of the reaction mechanism. Observations of Warburg that, at higher ozone concentrations, the quantum yield with ultraviolet light increases above two, indicate the presence of a chain reaction. The same conclusion must be drawn, on the basis of Kistiakowsky's experiments, for the reaction in visible light. However, the quantum yields in ultraviolet and visible light are not the same under otherwise identical conditions since the yield at 2530 Å. is ten times greater than at 6200 Å. We might note, in this connection, that experiments by Hibben [13] demonstrated a complete stability of ozone against the still smaller quanta of its infra-red absorption region.

At present little can be said definitively about the exact mechanism of the ozone reaction, since the equation calculated by Bodenstein [14] proved to be inconsistent with the experimental data.

The more recent results of Bodenstein and Kistiakowsky [15] support the latter's suggestion that the rate of reaction is only approximately proportional to the square root of ozone concentration and that this observed function has no kinetic meaning. The temperature coefficient of the ozone decomposition in ultraviolet light was found by Weigert [16] to be 1.15. Griffith and McKeown [17] arrived at the value 1.34 in visible light. Bodenstein and Kistiakowsky [18] found approximately the same value at high pressures, but observed that at very low (about 8 mm.) total pressures, that is, in the region where the rate of reaction is almost independent of the reactant concentration and where the quantum yield is close to 2.0, the temperature coefficient is much smaller, not far from unity. This observation probably indicates that, in the low pressure region, the mechanism of ozone decomposition is less complicated and possibly does not involve a chain reaction.

It has already been pointed out that the catalytic effects in ozone decomposition are not limited to the inhibitive action of indifferent gases. Weigert and Böhm [19] observed, for example, that on illumination by ultraviolet light of ozone in the presence of hydrogen, water is formed, but that simultaneously the decomposition of ozone is

[13] *Proc. Nat. Acad. Sci.*, 13, 626 (1927).
[14] *Trans. Farad. Soc.*, 21, 525 (1925).
[15] Unpublished.
[16] *Loc. cit.*, page 167.
[17] *Trans. Farad. Soc.*, 21, 597 (1925).
[18] Unpublished.
[19] *Z. physik. Chem.*, 90, 189 (1916).

markedly accelerated. Weigert [20] suggested subsequently that, in this case, the decomposition of ozone is, in reality, not a photochemical but a thermal reaction. He pointed out that, since ozone absorbs the ultraviolet rays very strongly, the reaction zone must be limited to a thin gas layer and that the heat liberated by the process

$$O_3' + H_2 = H_2O + O_2$$

will be sufficient to warm up this gas layer to a temperature at which the thermal decomposition of ozone proceeds at a measurable rate.

Griffith and Shutt [21] extended the experiments of Weigert and Böhm to visible light, obtaining concordant results. Weigert's theory, however, must be rejected, according to Griffith and Shutt, since, in visible light, where the reaction proceeds in the whole vessel, the temperature increase on illumination is not appreciably higher than in absence of hydrogen. Griffith and Shutt suggest therefore that water molecules formed in the reaction of activated ozone with hydrogen possess a high surplus energy and transfer it on collisions to ozone molecules, causing their secondary activation and subsequent reaction. An action of this sort must undoubtedly exist, since a comparison shows that the rate of ozone decomposition in the presence of hydrogen is even much faster than in the presence of helium, although with the latter the yield of inelastic collisions (comp. page 169) is very small. The acceleration in presence of hydrogen cannot be accounted for solely by the assumption that no degradation of primarily absorbed light energy takes place on inelastic collisions of activated ozone with hydrogen molecules.

Griffith and McWillie [22] demonstrated that, in presence of carbon monoxide, not only the decomposition of ozone by visible light but also a slow oxidation of the former to carbon dioxide takes place. The action of carbon monoxide differs from that of hydrogen in that the rate of ozone decomposition is only slightly accelerated. It is even possible to represent the experimental results of Griffith and McWillie by Equation 3 on page 169. The constant k' obtains thereby a value which lies between those of carbon dioxide and of nitrogen. The action of carbon monoxide on ozone decomposition is thus probably similar in nature to the action of indifferent gases, and the yield of inelastic collisions must lie between those in carbon dioxide and nitrogen.

The decomposition of ozone in presence of chlorine, when illumi-

[20] *Z. physik. Chem.*, 90, 223 (1916).
[21] *J. Chem. Soc.*, 123, 2752 (1923).
[22] *Loc. cit.*

nated by light of those wave lengths which are absorbed by chlorine, has been discussed in the chapter on photosensitisations.

Recently, Bodenstein, Hartek and Padelt[23] observed that the action of red light on chlorine-ozone mixtures differed greatly from the action of those shorter wave lengths absorbed by chlorine. Red light, absorbed mainly by ozone, causes a rapid formation of chlorine hexoxide Cl_2O_6 and the kinetics of this reaction do not show the simplicity characteristic of the photosensitised decomposition of ozone. These two reactions, so very different from one another, set up in the same gas mixture by light quanta of not considerably different energy content, are a particularly striking example of the importance, for the whole reaction mechanism, of the nature of those products which are formed in the primary light action.

Thermal Decomposition of Ozone. The kinetic interpretation of the photochemical reactions of ozone would undoubtedly be clarified by the knowledge of the mechanism of its thermal decomposition. So far, however, investigations of this latter reaction have not yielded unequivocal results. According to Warburg,[24] Clement,[25] and Chapman and Jones,[26] the reaction is of normal bimolecular type with a temperature coefficient which, substituted in the Arrhenius equation, yields about 26,000 cal. as necessary activation energy. Jahn,[27] however, found that the rate of thermal decomposition is retarded by oxygen. His result was confirmed by Pearman and Greaves.[28] Recently Griffith and McKeown[29] found that many indifferent gases can influence the thermal rate, although their effects are not identical with those on photochemical decomposition.

According to a suggestion of Christiansen,[29a] the phenomenon of inhibition of thermal reactions is a definite indication that they have a chain mechanism. A chain reaction, as the mechanism of ozone decomposition, obtains further support by the studies on the chemiluminescence of decomposing ozone. Stark's[30] original investigations and particularly the more recent experiments of Stuchtey[31] have definitely proved that chemiluminescence of ozone consists of numerous well defined bands extending from the visible far into the ultraviolet region, in fact even to below 2500 Å. where it requires quantum

[23] *Z. anorg. Chem.*, **147**, 233 (1925); see also, Kistiakowsky, *loc. cit.*, page 169.
[24] *Ann. Physik*, **9**, 1286 (1903).
[25] *Ibid.*, **14**, 334 (1904).
[26] *J. Chem. Soc.*, **97**, 2463 (1910).
[27] *Z. anorg. Chem.*, **48**, 260 (1906).
[28] *Proc. Roy. Soc.*, **80**, 353 (1908).
[29] *Proc. Farad. Soc.*, **21**, 597 (1925).
[29a] *J. Phys. Chem.*, **28**, 145 (1924).
[30] *Ann. Physik*, **43**, 319 (1914).
[31] *Z. wiss. Phot.*, **19**, 161 (1920).

energy in excess of 115,000 cal. The heat of bimolecular ozone decompositions is, on the other hand, approximately 64,000 cal.[32] which, even together with the activation energy of 26,000 cal., cannot account for the emission of these short waves. It thus becomes necessary to assume that the mechanism of ozone decomposition involves a transfer of energy from the reaction products to reacting molecules and its accumulation to relatively very large amounts.

The same conclusion must be drawn from recent experiments by Smyth [33] on inelastic collisions between slow moving electrons and decomposing ozone molecules. He found that collisions of the second kind take place in this case, whereby the excitation energy of ozone molecules is transformed into kinetic energy of translational electron movement. In the electron velocity distribution curve, Smyth observed three maxima at 0.52, 1.73, and 4.3 volts, which correspond to respectively 12,000, 40,000, and 111,000 cal. of transferred energy. These experiments are the most direct evidence of the suggested phenomenon of accumulation of large amounts of energy in single molecules during a thermal reaction.

Decomposition of Hydrogen Peroxide

The decomposition of hydrogen peroxide by ultraviolet light, studied thus far only in aqueous solutions, shows a marked analogy to ozone decomposition, as will be seen from the discussion which follows. For a long time, the decomposition of hydrogen peroxide by ultraviolet light as well as its stability against the similarly absorbed infra red radiation has been known.

More recently Tian [34] studied the kinetics of decomposition under the total radiation from a mercury lamp and obtained, at least in the case of lower concentrations, a unimolecular rate of reaction. He suggested, from this observation, that a proportionality existed between the light energy absorbed and the amount of hydrogen peroxide decomposed. Subsequently, however, Tian abandoned this suggestion as the result of his new measurements of the absorbed light energy [35] and concluded that the rate of reaction, instead of being proportional to the absorbed light energy, actually decreases with hydrogen peroxide concentration. Henri and Wurmser [36] estimated the quantum yield under the total radiation from a high tension spark discharge

[32] Jahn, *Z. anorg. Chem.*, **60**, 337 (1908).
[33] *Proc. Nat. Acad. Sci.*, **11**, 679 (1926).
[34] *Compt. rend.*, **151**, 1040 (1910).
[35] *Ibid.*, **156**, 1601, 1758, 1879 (1913).
[36] *Ibid.*, **156**, 1012 (1913).

and found a value of approximately 100 molecules of hydrogen peroxide per quantum of light energy absorbed. They also studied the spectral distribution of absorbed light and found that hydrogen peroxide solutions show an increasing absorption of wave lengths below 3000 Å. Later, they [37] repeated the measurements of the quantum yield in monochromatic light of different wave lengths and arrived at results which contradicted their earlier experiments, inasmuch as the quantum yield was now found to be only about 5. According to

TABLE 25. $H_2O_2 = 0.037N$.

Wave length	2800	2558	2300	2100 Å.
Light energy absorbed per decomp. molecule, ergs $\times 10^{-12}$	1.54	1.55	1.49	1.61
Quantum yield	4.4	4.9	5.7	5.9

Henri and Wurmser, their measurements, given in Table 25, indicate that it is not the number of quanta but the amount of absorbed light energy, independent of the wave length, which determines the rate of reaction. They further showed, varying the intensity of incident light, that a proportionality existed between this and the rate of reaction. The variation of the quantum yield with concentration of hydrogen peroxide was further studied by Kornfeld [38] in monochromatic light of approximately 3110 Å. wave length. Miss Kornfeld confirmed Tian's suggestion that the reaction velocity decreases with concentration, although this decrease was found to be rather slow. The measured quantum yields differ markedly from the more recent values of Henri and Wurmser, being about 80 in 0.5 N neutral solution of hydrogen peroxide and about 24 in 0.016 N solution.

In an attempt to interpret the discordance of the experimentally determined values for the quantum yield, Winther [39] recently suggested that the rate of hydrogen peroxide decomposition is not proportional to the incident light intensity and that, therefore, since different investigators were using light of different intensity, they could not have obtained concordant results. His suggestion is challenged by the experiments of Henri and Wurmser, given above, where the existence of this doubted proportionality is proved. Inasmuch as the disagreement is not due to experimental errors, we might connect it with the catalytic inhibition in the observed photochemical decomposition of hydrogen peroxide.

[37] *Compt. rend.*, 157, 126 (1913).
[38] *Z. wiss. Phot.*, 21, 66 (1921).
[39] *Trans. Farad. Soc.*, 21, 459 (1925).

Inhibition of the Decomposition of Hydrogen Peroxide. Originally, Henri and Wurmser [40] found that, in the presence of inorganic acids and alkali, the rate of photochemical decomposition is markedly retarded. Much more effective are such "catalytic poisons" as hydrogen sulfide, of which traces are sufficient to retard noticeably the rate of reaction. The subject was extended by Mathews and Curtis [41] including measurements on a number of organic substances, among which several strong inhibitors were discovered. They note that the influence of inhibitors on the rates of thermal and of photochemical reactions is in general different.

Miss Kornfeld [42] demonstrated that the effect of sulfuric acid is not due to a change of light absorption by hydrogen peroxide, since she obtained smaller quantum yields in presence of this acid. Since sodium sulfate was found to be completely ineffective, she concluded that the hydrogen ion must be the retarding agent.

A very complete and thorough study of the catalytic effects in hydrogen peroxide decomposition was carried out by Anderson and Taylor.[43] The inhibiting action of a large number of organic substances was found to be dependent generally on the spectral distribution of the effective radiation (varied by means of convenient ultraviolet light filters). A comparison between their results and the known [44] ultraviolet absorption spectra of the organic compounds investigated showed that, in a number of cases, the inhibition was largely due to the absorption of active radiation by these organic substances. Anderson and Taylor consider the action of organic acids, esters, amides and of quinine to be satisfactorily accounted for by the assumption of purely screening action, but point out that in the case of alcohols and basic amines some other explanation must be sought, since no simple correlation could be detected between their absorption spectra and their activity. They were able to confirm largely the earlier observations on the inhibition by inorganic compounds. The effect of alkali was found to be approximately 25 times stronger than that of acids. Of neutral salts only chlorides and, less strongly, bromides show the effect of inhibition. Anderson and Taylor demonstrated further that the inhibiting action of acids and alkali is reduced very markedly by neutral salts supplying a common ion. These observations indicate that the ions $H^{\cdot}$ and OH' are the effective

[40] *Compt. rend.*, 157, 284 (1913).
[41] *J. Phys. Chem.*, 18, 166, 521 (1914).
[42] *Loc. cit.*
[43] *J. Am. Chem. Soc.*, 45, 650, 1210 (1924).
[44] Comp., V. Henri, "Etudes de Photochemie," Paris, 1919.

agents and, furthermore, that the inhibiting action of the hydroxyl ion is approximately 25 times stronger than that of the hydrogen ion.

The inhibiting action was found to be independent of temperature, whereas the temperature coefficient of hydrogen peroxide decomposition rate was determined by Anderson and Taylor to be 1.43. The measurements of Miss Kornfeld yielded for this the value 1.32; those of Mathews and Curtis, 1.50.

Tian,[45] on the other hand, affirmed that the temperature coefficient was 1.15. Furthermore, his observations differ from the others in that he finds alkali to accelerate the rate of photochemical decomposition in the same way as it does the rate of thermal reaction.

Kornfeld [46] suggested that the light sensitive component in the decomposition is the hydrogen peroxide molecule and that the primary action of light consists in breaking it up into an hydroxyl ion, an energy-rich hydrogen ion, and an oxygen atom. This latter then causes the decomposition of a varying number of other hydrogen peroxide molecules. With the aid of some additional assumptions, Kornfeld was able to represent satisfactorily her own experimental results. The derived equation fails, however, to interpret the observations of Anderson and Taylor. These authors [47] pointed to the remarkable fact that even those organic inhibitors which show a pronounced parallelism between their activity and light absorption in different spectral regions, act more efficiently when present in the solution of the reactant than when in a separate screening solution. They claim that this phenomenon should indicate that the photochemical decomposition of hydrogen peroxide is accompanied by the emission and re-absorption of fluorescent light. This secondary radiation will likewise be absorbed by the inhibitors. They will therefore act in two ways when present in the solution: rob the solution of an amount of the primary irradiated energy, and also, by absorbing some of the secondary emission they will prevent a chain which normally would have been set up had a hydrogen peroxide molecule absorbed that secondary radiation. Anderson and Taylor further suggest that it is not the hydrogen peroxide molecule but the ion OOH' which is responsible for the photosensitivity of this reaction.

Heterogeneous Catalysis. The theory of hydrogen peroxide decomposition recently obtained a new development by the experiments of Rice,[48] who claimed that the submicroscopic dust particles, ordi-

[45] *Ann. Physique*, **5**, 248 (1916).
[46] *Loc. cit.*
[47] *Loc. cit.*
[48] *J. Am. Chem. Soc.*, **48**, 2099 (1926).

narily present in all hydrogen peroxide solutions, have a marked catalytic effect on the rate of photochemical decomposition. Rice believes that optically clear solutions, prepared by ultrafiltration and by other methods decompose at a rate which closely approximates the requirements of the equivalence law. He is even inclined to extend his theory by assigning an important rôle to the dust particles in many other photochemical reactions which are known to show marked deviations from the equivalence law. A further confirmation of these preliminary experiments will undoubtedly require a revision of the theories on the inhibiting actions in hydrogen peroxide and other decompositions and possibly demand interpretation involving anti-catalytic effects at the surface of dust particles.

A heterogeneous catalysis of a different type was discovered by W. Kistiakowsky [49] in the action of red and yellow potassium prussiate on the photochemical decomposition of hydrogen peroxide where the rate of decomposition was found to be accelerated autocatalytically. The decomposing action of the catalyst formed persisted even in the dark (the so-called photochemical after-effect). Kistiakowsky further demonstrated, with the aid of an ultramicroscope, that this catalysis is due to the action of a colloidal decomposition product of the iron cyanide complexes. The chemical nature of this decomposition product has not been definitely established. It is possible that, in presence of hydrogen peroxide, the decomposition of iron cyanide also leads to the formation of ferric hydroxide as was found to be the case for pure solutions of ferri- and ferro-potassium cyanide by Haber,[50] Foster,[51], and by Baudisch and Bass.[52]

Chlorine Water Decomposition

As early as 1785, Berthelot had found that aqueous solutions of chlorine are sensitive to light and that oxygen is evolved in the resulting reaction. Draper,[53] on the basis of his measurements on the rate of oxygen evolution, came to the conclusion that this reaction showed both an induction period and a marked after-effect. More recent research [54] attributes Draper's results to an over-saturation of the liquid by oxygen formed during illumination and its continued evolution in the dark.

In 1885, Wittwer [55] concluded that the rate of chlorine consump-

[49] *Z. physik. Chem.*, 35, 431 (1901).
[50] *Z. Elektrochem.*, 11, 846 (1905).
[51] *J. Chem. Soc.*, 89, 912 (1906).
[52] *Ber.*, 55, 2698 (1922).
[53] *Fortschritte der Physik*, 1845, 276.
[54] Comp. Allmand and co-workers, *J. Chem. Soc.*, 127, 822 (1925).
[55] *Pogg. Ann.*, 94, 597 (1885).

tion is proportional to the intensity of the radiation and can be expressed by a unimolecular velocity equation. His conclusions are in disagreement with those of Bunsen and Roscoe [56] and were challenged more recently by Billitzer,[57] who claimed that the rate of reaction is not proportional to light intensity. Furthermore, according to Billitzer, the reaction is autocatalytic. On the other hand, Benrath and Tuchel [58] represented their observations by a unimolecular velocity equation with fairly satisfactory results. All earlier investigators of the chlorine water decomposition believed that hydrochloric acid and molecular oxygen were the only products of reaction until Popper,[59] Gore [60] and Klimenko [61] demonstrated the formation of chloric acid in considerable quantities. Gore further claimed the formation of hydrogen peroxide, Richardson [62] suggested that the evolved oxygen is ozonised, and Billitzer [63] reported the production of perchloric acid.

In discussing the possible reaction mechanism Klimenko [64] suggested that dissolved chlorine is primarily hydrolysed according to the equation

$$Cl_2 + H_2O \rightleftarrows H\cdot + Cl^- + HOCl$$ [65]

and that the hypochlorous acid formed is decomposed on illumination according to:

$$3ClOH \rightarrow 2HCl + HClO_3.$$

His opinion that the hypochlorous acid is the only photochemically active component was shared by Jakowkin [66] and Dawson.[67] Billitzer [68] and Benrath and Tuchel [69] on the other hand believed that it is the non-hydrolysed chlorine molecule which becomes activated upon absorbing light. Recently Benrath and Schaffganz [70] advanced the opinion that the ion ClO^- is primarily responsible for the photosensitivity of chlorine water.

The reaction proceeds, according to Klimenko and Pekatoras,[71] to a quantitative completion and no stationary state is formed on illumination. The rate of reaction is strongly retarded by the addition

[56] *Pogg. Ann.*, 96, 373 (1855).
[57] *Chem. Z.*, 30, 1131 (1906); 31, 620 (1907).
[58] *Z. wiss. Phot.*, 13, 383 (1913).
[59] *Lieb. Ann.*, 227, 661 (1885).
[60] *Chem. News*, 57, 184 (1888).
[61] *Ber.*, 28, 2558 (1895). Also Pedler, *J. Chem. Soc.*, 57, 613 (1890).
[62] *J. Chem. Soc.*, 59, 536 (1891).
[63] *Loc. cit.*
[64] *Loc. cit.*
[65] See Jakowkin, *Z. physik. Chem.*, 29, 621 (1899).
[66] *Loc. cit.*
[67] *Z. wiss. Phot.*, 14, 213 (1914).
[68] *Loc. cit.*
[69] *Loc. cit.*
[70] *Z. physik. Chem.*, 103, 139 (1922).
[71] *Ibid.*, 4, 483 (1889).

of hydrochloric acid and to a somewhat less extent by chlorides. Klimenko and Petrenko [72] found, furthermore, that the inhibiting action of chlorides increases as the atomic weight of the cation. Benrath and Tuchel,[73] however, arrived at a different conclusion, claiming that only pure chlorine water decomposes quantitatively, while, in the presence of hydrochloric acid or chlorides, the reaction is incomplete. This result is astonishing inasmuch as the authors themselves had demonstrated that the reverse reaction did not exist; that is, there is no reaction between hydrochloric acid, oxygen and water under the action of light of the same wave lengths. They claim, moreover, that the inhibitive action of chlorides does not increase, but decreases with atomic weight of cation.

Milbaur [74] observed a retarding action on chlorine water decomposition by salts of heavy metals and attributed it to their inner filter action. On the other hand, he found molecular bromine had a positive catalytic effect, the catalytic action in this case being reciprocal, since Milbaur observed chlorine to accelerate the photochemical reaction of bromine with water. The temperature coefficient of the reaction is 1.4 according to Benrath and Tuchel.[75]

Allmand, Cunliffe and Maddison [76] studied the decomposition of chlorine and hypochlorous acid solutions in quartz vessels under the total radiation from a mercury lamp. According to these authors neither hydrogen peroxide, nor perchloric acid are formed in either of these photochemical reactions, the products being hydrochloric and chloric acids and molecular oxygen. Quantitative measurements were concerned chiefly with the chloric acid yield, in order to determine its dependence upon the various factors. The yield was unaffected by a variation in the concentrations of the reactants but was altered upon addition of hydrochloric acid or chlorides. A part of the results which were obtained is represented in Table 26, the yield being given in per cent of reacted chlorine or hypochlorous acid, identified in the form of chloric acid.[77]

The yields were the same in monochromatic light of the wave lengths: 4360, 3660 and 3230 Å. Solutions of sulfates scarcely affected the yield of chloric acid. Experiments with hypochlorous acid and sodium acetate indicated the presence of two simultaneous reactions:

[72] *Z. physik. Chem.*, **42**, 483 (1903); also Klimenko, *Ber.*, **28**, 2558 (1895).
[73] *Loc. cit.*
[74] *Z. physik. Chem.*, **86**, 564 (1914).
[75] *Loc. cit.*
[76] *J. Chem. Soc.*, **127**, 822 (1925).
[77] A yield of 100 per cent corresponds to the stoichiometric equations:

$$3HOCl \rightarrow 2HCl + HClO_3$$
$$3Cl_2 + 3H_2O \rightarrow 5HCl + HClO_3.$$

TABLE 26.

Reaction studied in:	Yield of chloric acid: Chlorine	Hypochlorous acid
H_2O	61.2 per cent	60.8 per cent
0.5*N* HCl	14.0 "	
0.5*N* KCl	29.0 "	
0.5*N* LiCl	39.0 "	
0.5*N* $CdCl_2$	44.6 "	
0.5*N* H_2SO_4	56.3 "	
5 per cent $HgCl_2$	64.1 "	
0.25*N* Na_2HPO_4		81 "

the formation of chloric acid and the halogenation of the acetic acid to trichloracetic acid. Allmand and his co-workers suggested that the hypochlorous acid is considerably more photosensitive than the chlorine molecule and that the primary reaction is

$$HClO + \text{light} \rightarrow HCl + O.$$

The oxygen atoms thus intermediately formed either recombine to form molecules or react with hypochlorous acid to give chloric acid. Since the equilibrium

$$Cl_2 + H_2O \rightleftarrows H^{\cdot} + Cl^{-} + HClO,$$

is established in the system, an addition of hydrogen or chloride ions will decrease the concentration of the hypochlorous acid and accordingly diminish the yield of chloric acid. The total rate of reaction will be similarly affected because the chlorine molecule is supposed to be less photosensitive than hypochlorous acid. If disodium hydrogen phosphate were added, it would depress the concentration of the hydrogen ions formed according to the above equilibrium; and the yield of chloric acid will therefore increase. This has been confirmed by experiment. The increase of the yield of chloric acid in presence of mercuric chloride is due to a decrease of chloride ion concentration on account of the formation of the complex ion $HgCl_4^{--}$.

Allmand and his co-workers pointed out, however, that all of these catalytic effects are only qualitatively accounted for by their theory. The calculated concentrations of the hypochlorous acid in the presence of various amounts of hydrochloric acid, and the yield of chloric acid, show a marked disproportionality, as will be seen from Table 27. They conclude from these data that chlorine molecules, too, must participate in some way in the reaction mechanism.

The Decomposition of Hypochlorite Ion. The photochemical decomposition of hypochlorite ion has been studied by Lewis [78] and his investigation extended by Spencer.[79] It was found that the decom-

[78] *J. Chem. Soc.*, 101, 2371 (1912).
[79] *Ibid.*, 105, 2565 (1914).

TABLE 27.

Solution	Fraction reacted on illumination	[HCl]	[Cl_2]	[HOCl]	Yield of $HClO_3$ per cent
0.5*N* Cl_2	0.45	0.0225	0.0275	0.0225	61
+ 0.01*N* HCl	0.35	0.0275	0.0325	0.0175	55
+ 0.1*N* HCl	0.04	0.102	0.048	0.002	29
+ 0.5*N* HCl	0.0015	0.500	0.0499	0.000075	14

position is caused by the spectral region 4360-3130 Å. of a uviol mercury lamp. The order of reaction in total radiation is between 1 and 0. Spencer suggests that the rate of reaction is proportional to the absorbed light energy and that the indefinite order is due to a gradually increasing absorption of shorter waves by a hypochlorite solution. Experiments in monochromatic light demonstrated that the wave length 4050 Å. which is only weakly absorbed, actually causes a strictly unimolecular rate, whereas in the light of the wave length 3130 Å. the reaction is approximately of zero order. Spencer finds, further, that the photochemical efficiency of incident radiation increases with decreasing wave length. The question must be left open as to whether this effect is entirely due to an increasing absorption of shorter wave lengths by the hypochlorite ion. The rate of decomposition was found to be faster in neutral solutions of sodium hypochlorite, although the presence of free alkali has not a very great retarding influence. Even less pronounced is the retardation of sodium chloride, the rate of reaction being decreased by about 10 per cent on addition of 0.34 *N* NaCl. The temperature coefficient of the hypochlorite ion decomposition, as determined by Spencer, is equal to 1.06, and differs markedly from the value 1.4 given by Benrath and Tuchel [80] for chlorine water. However, it is possible that this difference is due to the action of secondary factors such as a variation of hypochlorous acid concentration with temperature in the latter's experiments.

According to Allmand,[81] Holmes found that, in addition to oxygen and chloride ion, chloric acid is one of the products of hypochlorite ion decomposition. The yield of chloric acid is much smaller, however, than in the case of chlorine water decomposition and amounts to about 10-12 per cent of the theoretical yield. Allmand interprets these facts by suggesting that the primary action of light on hypochlorite ion results in the formation of free oxygen atoms but that hypochlorite ion is a less active acceptor for them than is hypochlorous acid. On the other hand, he reports that preliminary experiments indicate iden-

[80] *Loc. cit.*, page 178.
[81] *Loc. cit.*, page 179.

tical quantum yields in the decompositions of chlorine water, hypochlorous acid and hypochlorite ion.

The photochemical decompositions of oxyhalogen compounds other than those we have discussed have been studied more or less qualitatively by Oertel,[82] by Mathews and Curtis,[83] and by others.

Eder's Solution

Very complicated kinetic relations have been observed by numerous investigators in the photochemical decomposition of the so-called Eder's solution, a mixture of mercuric chloride and ammonium oxalate. Eder [84] observed the formation of a precipitate of mercurous chloride upon illumination of this mixture by sunlight. According to him, the reaction is represented by the stoichiometric equation:

$$2HgCl_2 + (NH_4)_2C_2O_4 \rightarrow Hg_2Cl_2 + 2NH_4Cl + 2CO_2.$$

The formation of mercurous chloride does not set in instantaneously upon illumination, but rather requires a certain induction period, interpreted by Eder as the time necessary for the solution to become saturated with the slightly soluble mercurous salt. Apart from this complicating circumstance he considered the photochemical reaction to be a very convenient system for actinometric purposes. Unfortunately, subsequent investigations revealed an extraordinary multitude of catalytic effects to which the reaction is subject and thus demonstrated the inconvenience of its use in the way suggested by Eder. Kastle and Beatty [85] showed that the rate of mercurous chloride formation is accelerated in presence of ferric and uranyl salts and of some other substances, but is retarded by chromic acid and its salts. Gros [86] found that Eder's reaction proceeded at a much higher rate when small quantities of fluorescein were present in the solution. Jodlblauer and Tappeiner [87] extended his experiments and demonstrated that a large variety of dyestuffs exhibited analogous properties. According to these authors, however, only fluorescent dyestuffs act as photosensitisers of the reaction, whereas those which do not fluoresce have practically no effect on the rate of mercurous chloride formation in sunlight. They also discovered that oxygen exerts a strong inhibitive action on the rate of photochemical reaction.

In a series of publications, Winther [88] dealt with the different

[82] *Biochem. Z.*, 60, 480 (1914).
[83] *J. Phys. Chem.*, 18, 641 (1914).
[84] *Wien. Akad. Ber.*, 2 (1879).
[85] *J. Am. Chem. Soc.*, 24, 182 (1900).
[86] *Z. physik. Chem.*, 37, 192 (1901).
[87] *Ber.*, 38, 9602 (1905).
[88] *Z. wiss. Phot.*, 7, 409 (1909); 8, 197 (1910); 9, 205 (1911).

catalytic phenomena discovered by earlier investigators, directing, however, his attention mainly towards the action of ferric salts and of oxygen. He was able to confirm the observations of Kastle and Beatty on the accelerating action of ferric salts and to show that these accelerate the rate of mercurous chloride formation only when present in small quantities. Indeed, sufficiently high concentrations of ferric chloride completely inhibit the photochemical reaction. The optimum concentration, which causes a rate of mercurous chloride formation some hundred times more rapid than that of a pure Eder's solution, is dependent on the concentration of oxygen dissolved in the liquid. In solutions saturated by air, the maximum rate is attained at a concentration 1.7×10^{-3} molar with respect to ferric salt; whereas, in solutions carefully freed from oxygen by a stream of carbon dioxide,[89] the maximum has already been reached at 1.7×10^{-4} molar concentration.

On the other hand, the retarding action of oxygen is dependent on the concentration of ferric salt, as will be seen from Table 28.

TABLE 28.

	Relative rate of Hg_2Cl_2 formation		
	Solution:		
$FeCl_3$ in mols per liter	free of oxygen	saturated by air	Ratio
2.8×10^{-4}	1000	158	6.3
2.8×10^{-5}	910	18	52.0
7×10^{-6}	400	4.4	90.0
0.0	160	0.16	1000.

Although Winther's experiments were undoubtedly not very precise, the decrease of retarding action of oxygen at higher concentrations of ferric salt can hardly be denied. In fact, at very high concentrations of the latter (10^{-2} N), Winther even claimed that oxygen accelerated the rate of reaction.

Since oxygen is used up during the course of this reaction, the rate of mercurous chloride formation plotted against time of illumination shows an autocatalytic increase in solutions originally saturated with oxygen. In oxygen-free liquids the "order" of the photochemical reaction with respect to mercuric chloride and ammonium oxalate, is about two, but is probably dependent on the ferric ion concentration.

Winther found that Eder's solution, when most carefully purified from iron salts, absorbs only light below *circa* 3130 Å. On the other hand, the light sensitivity of a fairly pure solution has already begun

[89] Jodlblauer and Tappeiner demonstrated that this latter has no specific action of its own.

at 5000 Å. These observations led Winther to the conclusion that the sensitivity to longer waves is entirely due to minute quantities of ferric salts. In fact, he believed that even the short wave lengths absorbed by a pure solution of mercuric chloride and ammonium oxalate do not act photochemically unless ferric salt is present in the solution. This last suggestion of his has received very insufficient experimental support. His concept of the reaction mechanism is based on the following additional observations. Winther found that, in solutions containing oxalate ions, the trivalent ferric ions are reduced by action of ultraviolet and visible light to the bivalent ferrous ion. Furthermore, he observed that ferrous salts cause a formation of mercurous chloride from Eder's solution in the dark at room temperature. The kinetics of this reaction are rather complicated and oxygen plays an important rôle in retarding the rate. The conclusion which Winther drew from these and previous observations was that the primary light action consists merely in reduction of the ferric oxalate present. He assumes that this reaction is independent of the oxygen concentration. The formation of mercurous chloride is actually caused by a secondary, purely thermal, reaction of ferrous ions, which is retarded by oxygen and exhibits the other anomalies above described. It is useless to enter into a detailed discussion of Winther's theory, since he has completely overlooked a very important aspect of the whole problem. It is well established that, in aqueous solutions, ferric chloride is hydrolysed to a great extent and that, consequently, such solutions must contain a higher concentration of hydrogen ions. Now Roloff [90] had previously found these ions to be a strong inhibitor of the photochemical reaction in Eder's solution. A calculation shows that, under Winther's experimental conditions, the retardation of the reaction rate by high concentrations of ferric chloride is due, if not entirely, at least in a large degree to the hydrogen ions formed in the hydrolysis of the ferric salt. Roloff showed that, besides hydrogen ions, chloride ions show a similar retarding influence, whereas potassium nitrate in small quantities accelerates the rate of reaction. He suggested, consequently, that the reaction in Eder's solution is one between the mercuric and oxalate ions. An application of the mass action law shows that the concentrations of the supposed reactants must be decreased by chloride or hydrogen ions. Hence, these are inhibitors. An explanation of the potassium nitrate action, similarly based on the application of the mass action law to ionic equilibria, was likewise

[90] *Z. physik. Chem.*, 13, 327 (1894).

advanced by Roloff. Winther,[91] however, failed to observe an acceleration in the reaction rate by this salt and, criticising Roloff's theory, called attention to the known absorption of ultraviolet light by nitrate ions as a second source of their influence on the reaction rate in Eder's solution, that is, by their screening action. Later, Berger [92] pointed out that the decomposition of nitrate by ultraviolet light, followed by the formation of molecular oxygen, may cause further complications in Eder's reaction in presence of this salt. Berger carried out a systematic study of the effects of electrolytes on the rate of mercurous chloride formation. The results are represented in Figure 3, where the relative rate of reaction is plotted against concentration of salts and acids added. Figure 4 shows the results of Berger on the action of ferric and uranyl salts and also the curve obtained by Roloff on the action of potassium nitrate. It is apparent that, whereas the effect of ferric salts is already noticeable at very small concentrations, the action of uranyl salts and of nitrate is some hundred times less pronounced, although the general shape of the curve is unchanged. The ferric chloride curve is in marked disagreement with Winther's earlier results. Berger used solutions saturated by air and found the optimum concentration of ferric salt at *circa* 3×10^{-3} M against 1.7×10^{-3} M of Winther. Still more astonishing is the fact that, while Berger obtained only a threefold increase of the reaction velocity at this concentration, Winther recorded a hundredfold acceleration. The reasons for this discordancy cannot be definitely assigned. It would be well to point out, however, that Berger examined the reaction under the total radiation from a mercury lamp, transmitted by quartz, whereas Winther used sunlight and glass vessels almost exclusively. It is therefore possible to attribute the disagreement to a difference of effective wave lengths employed under two different experimental conditions. Another possibility, not excluded *a priori*, is that Berger had, from the beginning, a solution containing noticeable amounts of ferric salts as impurity, thus showing an increased reaction ability.

In the interpretation of the effects of electrolytes, as represented in Figure 3, Berger pointed out that Roloff's theory based on the classical concept of electrolytic dissociation is inadequate for a relevant explanation of differences in the action of single salts. Accordingly, Berger linked the modern theory of complete dissociation of strong electrolytes of Debye [93] with the theory of ionic catalysis of

[91] *Loc. cit.*
[92] *Rec. trav. chim.*, 40, 387 (1921).
[93] *Physik. Z.*, 24, 185, 306 (1923).

Brönsted,[94] suggesting that the observed inhibition by electrolytes is mainly due to electrostatic forces of ionic charges. Berger's theory and its applications will be discussed later on in connection with other experimental evidence. At this point it may be remarked with respect to Eder's solution that Berger completely neglects the effects of ferric salts and of oxygen and their possible influence by variations in neutral salt concentration.

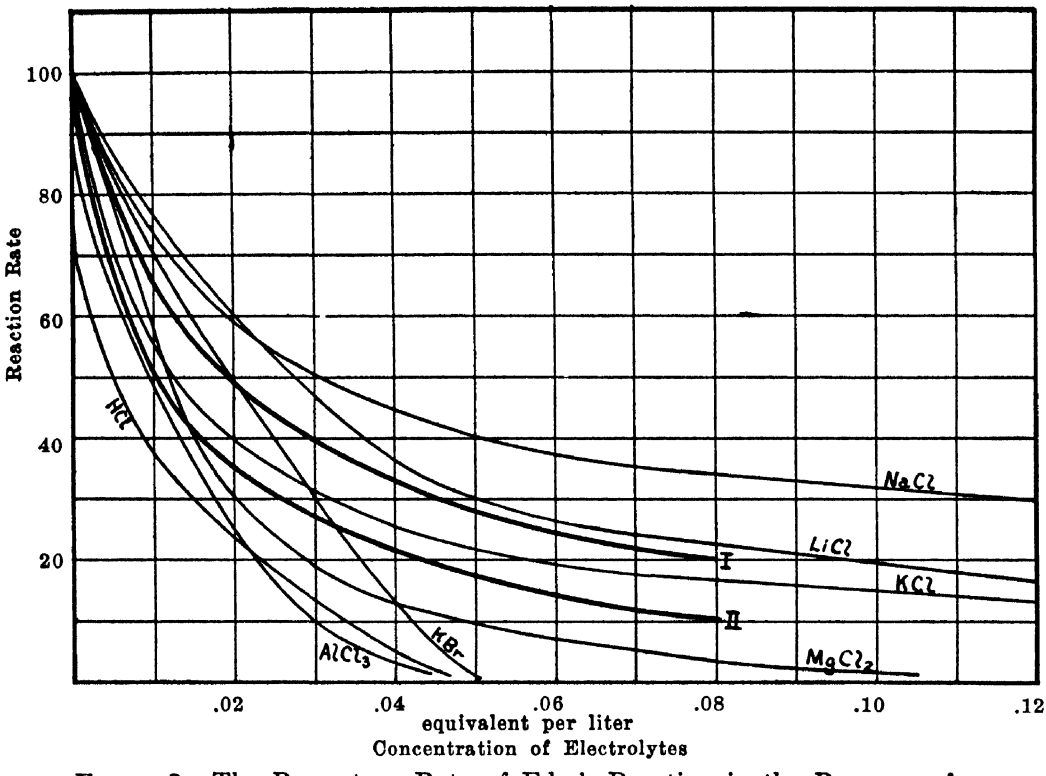


FIGURE 3.—The Percentage Rate of Eder's Reaction in the Presence of Electrolytes.

The investigation of Winther on the photosensitising action of dyestuffs on Eder's solution[95] yielded sparse results. He demonstrated, however, that the light sensitivity can be shifted to longer wave regions in agreement with the absorption spectra of the dyes employed. In a subsequent investigation, Winther and Oxholt-Howe[96] showed that eosin used as photosensitiser is partly decomposed by light and that the substances formed act as inhibitors of Eder's reaction. The temperature coefficient of a pure solution had been found by Eder[97] to be 1.24 in sunlight. Padoa and Minganti[98] established, however,

[94] *Z. physik. Chem.*, 102, 169 (1922).
[95] *Loc. cit.*
[96] *Z. wiss. Phot.*, 13, 89 (1914).
[97] *Loc. cit.*
[98] *Atti accad. Lincei*, 24, 97 (1915).

that the temperature coefficient of Eder's reaction is a function of the wave length of incident radiation. It increases from 1.05 in the spectral region 2800-4000 Å. to 1.21 in the light of the wave length 4480 Å. and even to 1.75 when Eder's solution is made sensitive to

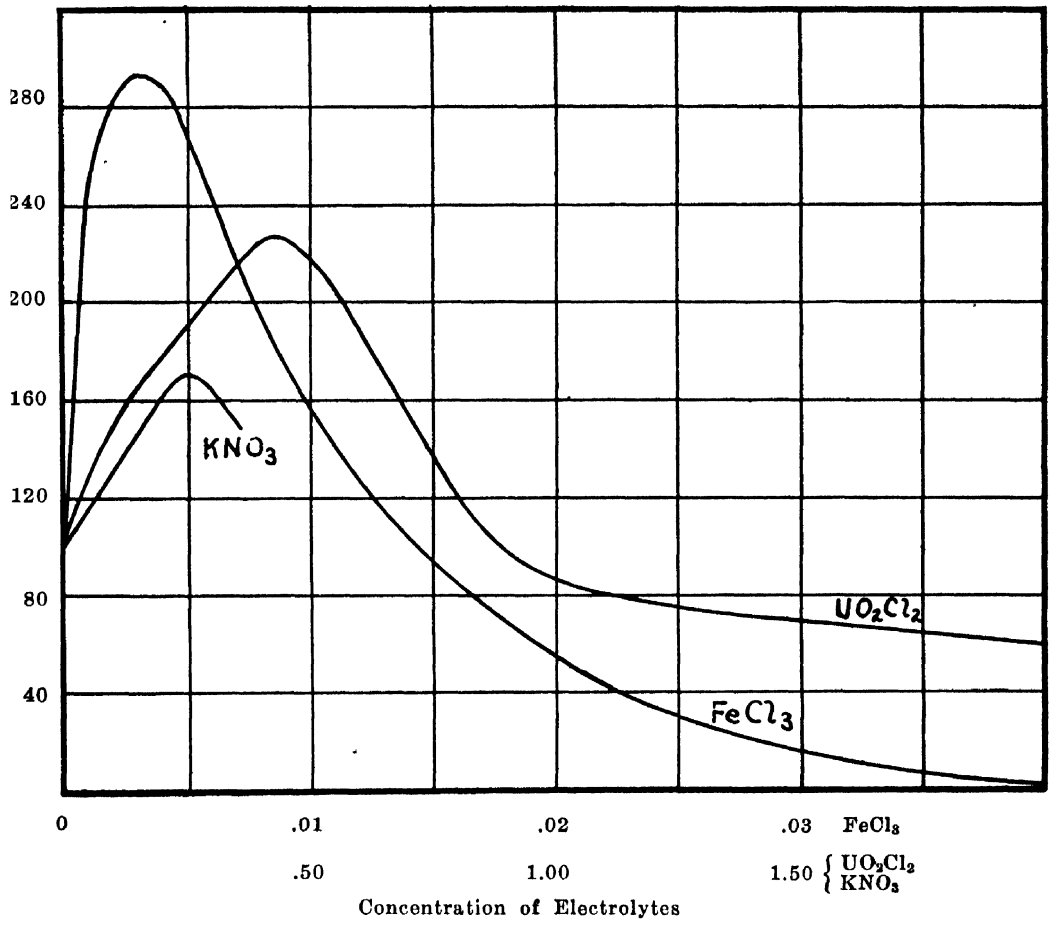


FIGURE 4.—The Relative Rate of Eder's Reaction in the Presence of Electrolytes.

green light by tetrabromofluorescein. These effects will be the object of discussion in the next chapter.

REACTIONS OF COBALTIC COMPLEXES

The photochemical reactions of complex cobaltic salts have been investigated so far only very incompletely. The best known reaction is that of complex potassium cobaltic oxalate originally studied by Vranek.[99] He discovered that this complex cobaltic salt was de-

[99] *Z. Elektrochem.*, 23, 336 (1917).

composed by ultraviolet and violet light into cobaltous oxalate and potassium oxalate. The rate of reaction, measured in very dilute solutions, was found to be approximately proportional to the absorbed light energy, at least in the concentration interval 0.005-0.0002 *M* and in the initial stages of illumination. As the reaction proceeds, however, its rate is retarded by the potassium oxalate which is being formed. Dilute acids have, according to Vranek, practically no effect on the rate of reaction. The absorption spectrum of cobaltic oxalate, as studied by him, consists of two well defined bands with absorption maxima at about 6050 and 4260 Å. He demonstrated, however, that not all absorbed wave lengths are photochemically active, but only those below *circa* 4900 Å. Measurements of quantum yield indicate that it rapidly increases with decreasing wave length, as will be seen from Table 29.

TABLE 29.

Decomposition of cobaltic oxalate.

Wave length	4920	4360	4050	3660 Å.
Quantum yield	0.0	0.6	0.9	1.5

Vranek pointed out that the three higher values, when plotted against wave length, lie on a straight line. Its continuation indicates a quantum yield zero at a wave length close to 4900 Å., as was actually confirmed by experiments. In the photochemical decomposition of cobaltic oxalate, therefore, we encounter one of those reactions in which the relation between reaction velocity and wave length of incident radiation is in disagreement with the quantum laws of light absorption, as emphasised in the equivalence law. Vranek pointed out this important result of his investigation without attempting to find a relevant explanation for it.

The temperature coefficient of the photochemical decomposition of cobaltic oxalate, according to Vranek, has a very small value: 1.06, which is in contrast with the large value, 4.2, of thermal reaction.

Jaeger and Berger [100] studied the influence of neutral salts on the rate of cobaltic oxalate decomposition in solutions more concentrated than those of Vranek. They found that the latter's observations on the retarding influence of potassium oxalate, and on the approximate proportionality between the initial reaction rate and the absorbed light energy, held as well in their own working range, a concentration interval 0.04-0.1 *M* potassium cobaltic oxalate. The effect of neutral salts was quite noticeable, as will be seen from Figure 5, in which the

[100] *Rec. trav. chim.*, 40, 153 (1921).

percentage decomposition under identical conditions of illumination is plotted against the concentration of neutral salts.

A comparison with Figure 3, representing similar effects in Eder's reaction, shows that not only has the shape of the curves been entirely changed, but also the average activity of electrolytes in influencing the reaction rate has been reduced manyfold, as indicated by the higher concentrations of the salts necessary in the latter case to produce noticeable effects.

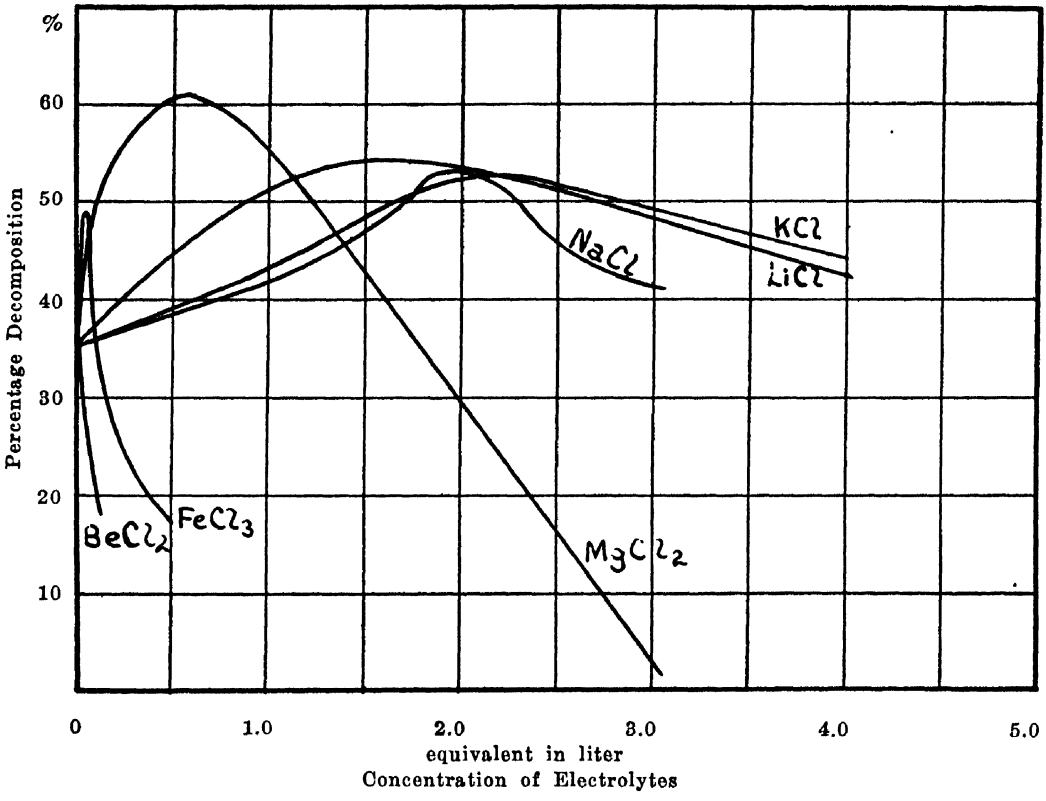


FIGURE 5.—The Rate of Decomposition of $[Co(C_2O_4)_3]K_3$ in the Presence of Electrolytes.

Schwartz and Weiss [101] examined the effect of light on the different complex cobaltic amino-nitrites in aqueous solution. Violet and ultraviolet light were found to cause a decomposition and Schwartz and Weiss assume the reactions to be pure hydrolysis, as for instance:

$$Co(NH_3)_3(NO_2)_3 + 3H_2O \rightarrow Co(OH)_3 + 3NH_4NO_2.$$

The course of a decomposition follows more or less exactly a unimolecular velocity equation, but experiments with different concentrations indicate a reaction of zero order. This behaviour, being

[101] *Ber.*, 58B, 746 (1925).

similar to that of complex potassium cobaltic oxalate, permits the conclusion that the reaction products retard the rate of decomposition. The light sensitivity of members of this class of complex cobaltic salts increases with the number of nitrite groups present in the molecule. Unfortunately, the experiments of Schwartz and Weiss offer no criterion as to whether the increased sensitivity is due to a greater absorption of light energy or to the increase in quantum yield of corresponding reactions. The second possibility is, however, more in accord with the experimental arrangement of Schwartz and Weiss and with the absorption spectra of cobaltic complexes. They established a relationship with respect to spectral sensitivity of all of the investigated cobaltic amino-nitrites similar to that observed by Vranek for cobaltic oxalate: the mercury line 4920 Å. is still practically inactive photochemically and the light efficiency apparently increases towards the shorter wave lengths. The lack of energy measurements at present makes an exact calculation of the quantum yields in different spectral regions impossible.

Recently, Berger [102] demonstrated that the photochemical decomposition of various complex cobaltic salts is a reduction of the trivalent cobalt atom and not a hydrolysis, as was suggested by Schwartz and Weiss. The resulting cobaltous hydroxide is then, however, rapidly oxidised by oxygen of the air to cobaltic hydroxide. Berger's experiments were carried out in dilute acid solutions and comprised a number of cobaltic salts containing NO_2, C_2O_4, NH_3 and C_2H_4 groups in the complex. Of these, the first two were found to cause a particularly pronounced sensitivity to light.

The efficiency of electrolytes in influencing the reaction rate was found to be of the same order of magnitude as in the decomposition of cobaltic oxalate. The shape of the curves obtained is, however, entirely different. In the case of negative complexes like $[Co(NH_3)_2(NO_2)_4]\ NH_4$ a decrease of the reaction velocity is usually followed by an increase, with the minimum lying at 2 to 6 moles per liter concentration of the salt, depending on its nature. The decomposition of positive complexes like $[Co(NH_3)_5(NO_2)]\ Cl_2$ is retarded throughout the whole interval of salt concentrations (0 to 8 mols per liter), the salt effect being particularly pronounced at higher concentrations. Berger finds, however, several exceptions to this rule. The relative activity of different salts varies from complex to complex, haphazardly, with the exception of nitrates, which show, for all decompositions, the most pronounced inhibiting action.

[102] *Rec. trav. chim.*, 44, 49 (1925).

Berger's Theory of Salt Effect. It was mentioned above that Berger developed a theory of ionic catalysis of photochemical reactions and applied it to the experimental data. He drew a rather sharp distinction between three groups of photochemical reactions in solutions. To the first belong those reactions which are particularly sensitive to the presence of electrolytes such as Eder's solution. Berger added another example when he showed that inhibition by salts in uranyl formate decomposition is of the same order of magnitude, although every salt has a different effect in both reactions. Complex cobaltic salts belong to the second group. The inhibition by neutral salts, although noticeable, becomes pronounced only at high salt concentrations. Finally the isomeric change of o-nitrobenzaldehyde [103] into o-nitrosobenzoic acid represents the third group, where even the highest concentrations of electrolytes do not affect the reaction velocity by more than a few per cent. Possibly, the decomposition of oxalic acid belongs to this class, since Benrath and co-workers [104] find the neutral salt effect so small that it is practically negligible. Berger pointed out that reactions of the first group are probably reactions between simple ions, those of the second group involve changes in large complexes, whereas reactions of neutral molecules constitute the third group. In accounting for the high sensitivity of ionic reactions to the presence of foreign ions, Berger combines the theory of Debye and Hückel [105] of complete dissociation of electrolytes with the expression suggested by Brönsted [106] for the rate of thermal reactions

$$(1)\quad \frac{dc}{dt} = k.c_1^{n_1} c_2^{n_2} \ldots F$$

$$(2)\quad F = \frac{f_1^{n_1} f_2^{n_2} \ldots .}{f_0}$$

In these equations c_1, c_2, etc., represent the concentrations of the reacting ions, f_1, f_2, etc., their activity coefficients. Brönsted assumed that reactions in solutions generally proceed through an intermediary formation of a "critical complex" by the reactants. He took account of this assumption by introducing into the expression for the reaction velocity an activity coefficient of this hypothetical complex f_0. It must be remarked here that Brönsted's velocity equation, although lacking a complete kinetic interpretation, yielded remarkable agreement with numerous observations on the rate of thermal reactions and on their catalysis by ions. This last effect directly follows from

[103] See page 51.
[104] *Z. wiss. Phot.*, 22 (1925).
[105] *Loc. cit.*
[106] *Loc. cit.*

Brönsted's theory, since the presence of electrolytes in the reacting solution necessarily affects the activity coefficients of the reactants and of the "critical complex."

Berger applied Brönsted's theory *in toto* to photochemical reactions, adding the assumption that, in such cases, the formation of the "critical complex" is due to the absorbed light energy. The effect upon adding electrolytes, as interpreted by Brönsted, is calculable on the basis of Debye's theory, in so far as ionic charges of the reactants and of the critical complex are known. Berger therefore calculated the theoretical effect of electrolytes on Eder's reaction, assuming that the velocity-determining process is: $Hg \cdot + C_2O_4^{--} \longrightarrow$ critic. compl. (HgC_2O_4). He thus assumes two bivalent ions form an uncharged complex, hence a complex, the activity coefficient of which is close to unity. In Figure 3 the curves I and II represent the calculated effect of electrolytes with two monovalent ions (KCl) and of those with one bivalent and two monovalent ions ($MgCl_2$) respectively. In the case of the decomposition of uranyl formate Berger assumes that it proceeds in two stages:

$$\text{I} \quad UO_2(HCOO)_2 + HCOOH \rightarrow UO(HCOO)_2 + CO_2 + H_2O$$
$$\text{II} \quad UO(HCOO)_2 + 2HCOOH \rightarrow U(HCOO)_4 + H_2O$$

Of these, the first determines the reaction velocity. Again the critical complex is neutral, but in this case is composed of the following ions:

$$UO_2^{\cdot\cdot} + H^{\cdot} + 3HCOO^{-},$$

and therefore according to Brönsted's theory a different effect of electrolytes should be anticipated.

Although the agreement between calculated and observed values is fairly satisfactory in both reactions for the uni-univalent chlorides; it is less so for the bi-univalent electrolytes, as $MgCl_2$; and the theory seems to fail completely in the cases (see Fig. 3) of hydrogen chloride and of potassium bromide. In discussing these deviations, Berger points out that Brönsted's theory must be regarded as a first approximation only and that actually, in addition to the charge, the size, hydration, etc., of single ions should be considered in calculating their catalytic influence.

Berger's interpretation of Eder's reaction fails completely to take into account the action of ferric salts, although Winther's experiments demonstrate conclusively that, at least in longer wave regions, these and not mercuric or oxalate ions are the light sensitive component. Furthermore, a rough estimation of the absorbed light energy shows that Eder's reaction must have a chain mechanism, because

many molecules of mercurous chloride are formed, at least in oxygen free solutions, per absorbed light quantum. It is of course quite possible that it is not the primary photochemical reaction which is sensitive to the presence of electrolytes as Berger proposed, but the secondary thermal processes constituting the chain mechanism. If this suggestion is proved by experiments, Berger's observations will become merely additional evidence of the purely thermal character of those reaction chains which so often follow the primary photochemical process. Little can be said on the decomposition of uranyl formate. The measurements of the quantum yield [107] rather indicate the absence of a chain mechanism, although a quantum yield less than unity does not exclude its possibility *a priori*. Berger's interpretation of the reaction mechanism appears somewhat arbitrary, and is not sufficiently confirmed by the only approximate agreement which he obtains between calculated and measured ionic catalysis.

In interpreting the complex cobaltic salt decompositions Berger pointed out that the photochemical process is probably localised within the complex. Consequently, he concludes that the influence of electrolytes is probably not due to any change in activity coefficient of the whole complex. He assumes instead that, *ceteris paribus*, the reaction velocity is proportional to the activity coefficient of the salt solution itself. By this assumption at least a qualitative explanation of the catalysis curves follows in the reaction of negative cobaltic complexes, since, as is well known, the activity of electrolytes passes through a minimum in that interval of concentration which was studied by Berger. In order to explain the catalysis in the reaction of positive complexes and to attain a closer agreement between theory and experiment for negative complexes, Berger makes an additional assumption: a specific action on the reaction velocity by the ions attracted to the charged complexes. Negative ions attracted by positive complexes are supposed to increase the stability of the latter, and thus decrease the reaction velocity throughout the whole concentration interval. On the other hand, the stability of negative complexes is lessened by the proximity of positive ions. The results on the ionic catalysis of cobaltic-oxalate decomposition do not satisfy either of these two possible types of ionic action and he therefore suggests that the peculiar shape of the curves obtained is due to an additional thermal catalysis of the relatively unstable cobaltic oxalate complex by the electrolytes. From this discussion it is evident that, for even a qualitative interpretation of observed phenomena, Berger's

[107] See page 149.

theory in its present state involves several insecure assumptions. However, his most important conclusion, namely, that the salt catalysis of photochemical reactions is due mainly to ionic charges can hardly be doubted and thus constitutes an interesting contribution to the study of photochemical kinetics. The question as to whether the electrolytes actually influence the decomposition rate of the primary products of light action, as was assumed by Berger, or whether they affect the rate of the secondary chain reactions, thereby altering the average length of the chains, has not yet been decided experimentally.

Reduction of Ferric Salts. The photochemical reduction of ferric ions by oxalic acid, which, according to Winther, plays such an important rôle in the mechanism of Eder's reaction, had already been noticed by Eder.[108] The latter discovered that sunlight causes an analogous reaction when, instead of oxalic acid, succinic, tartaric, citric and some other organic acids are present in the solution. Later, Benrath,[109] working with concentrated solutions, found a reaction of zero order in all cases. More extensive measurements on the four organic acids mentioned above were carried out by Winther and Oxholt Howe.[110] Their experiments revealed unusual relationships, but, unfortunately, a very inaccurate analytical method was employed in determining the reaction velocities, so that most of their results are quite uncertain. With monochromatic illumination (wave lengths 4360, 4050, 3660, 3130 Å.) the ensuing reaction rate was found to be of zero order in solutions containing 0.1 *M* organic acid and 0.006-0.0006 *M* ferric chloride. On the other hand, the light absorption by ferric salts of this concentration was found to be incomplete in the spectral region investigated. These two observations, when combined, indicate an autocatalytic effect, since the amount of ferric salt and therefore of light energy absorbed decreases during the course of the reaction. It was also found that the rate of reaction was proportional to the initial ferric chloride concentration, but that the light absorption coefficients of solutions with all four organic acids showed a steady increase with decreasing ferric chloride concentration. Thus, reduced to equal amounts of light energy absorbed, the rates of decomposition diminish with decreasing ferric chloride concentration.

Measurements of quantum yield indicate a chain mechanism reaction since more than one ferric ion is reduced when one light energy quantum is absorbed. The yield, under otherwise identical condi-

[108] *Sitzb. Wien Akad.*, **82**, II, 606 (1880).
[109] *Z. physik. Chem.*, **74**, 115 (1910).
[110] *Z. wiss. Phot.*, **14**, 196 (1913).

tions, varies inversely as the light absorption coefficients of the solutions at different wave lengths. Thus, for example, the wave length 4360 Å., which in all solutions is less strongly absorbed than the wave length 4050 Å., causes a higher quantum yield. The theory advanced by Winther and Oxholt Howe essentially states that at least two different light absorbing molecular species containing ferric ion are present in the solutions being studied and that the light energy absorbed by only one of them is utilised for the photochemical process, whereas the remainder is transformed into heat energy. The observed marked deviations from Beer's absorption law undoubtedly support the theory of there being several light absorbing compounds in these solutions of organic ferric salts. A discussion of the detailed applications of this theory will, however, be omitted here on account of the very inexact experimental data, making a critical survey impossible.

Autoxidations

We shall turn, now, to the discussion of a group of photochemical reactions in solution which all involve the process of oxidation by dissolved oxygen. Since the latter, at moderate concentrations, does not absorb radiation, except in the extreme ultraviolet (below 2000 Å.), the various oxygen acceptors we shall discuss must obviously be the light absorbing components. As might be expected, these different light absorbing molecules cause divergent kinetics for the resulting reactions. They have one feature in common, however: practically all of them involve some kind of chain mechanism as revealed by measurements on quantum yield, and consequently they exhibit a large variety of catalytic effects.

Oxidation of Sodium Sulfite. The thermal oxidation of sodium sulfite solutions has been the object of repeated investigations by Bigelow,[111] Titoff,[112] Moureu and Dufraisse [113] and others. Originally, Bigelow had noted the strong inhibitive action of many organic compounds and had demonstrated that the inhibition was not due to a retardation of solution of oxygen but to the influence on the rate of reaction between oxygen and sulfite. Titoff confirmed these results and called attention to the fact that copper salts are powerful accelerators of the reaction. In accordance with Titoff's experimental results, Luther [114] developed the theory that the inhibitors acted by

[111] *Z. physik. Chem.*, 26, 493 (1898); 12, 329 (1893).
[112] *Ibid.*, 45, 641 (1903).
[113] *Compt. rend.*, 174, 258 (1922); 175, 127 (1922); 176, 624, 797 (1923); 178, 824, 1498, 1861 (1923); 179, 237 (1924); also *Solvay Reports*, Apr., 1925, p. 524.
[114] *Z. physik. Chem.*, 45, 662 (1903).

destroying the positive catalysts simultaneously present. Moureu and Dufraisse, however, concluded that his theory does not account for their own experimental results. They suggest, supported by earlier observations, that normally oxidations by free oxygen proceed through an intermediary formation of an unstable peroxide and that inhibitors act by destroying this peroxide. Moureu and Dufraisse advanced, as alternative mechanisms for such inhibitions, the schemes

$$\text{I} \quad A + O_2 \rightarrow AO_2;\ AO_2 + B \rightarrow AO + BO;\ AO + BO \rightarrow A + B + O_2$$
$$\text{II} \quad A + O_2 \rightarrow AO_2;\ B + O_2 \rightarrow BO_2;\ AO_2 + BO_2 \rightarrow A + B + 2O_2$$

in which A denotes the oxidisable substance and B the inhibitor. In both cases the reactants, after a sequence of interactions, return to the original state of unoxidised molecules and of free oxygen.

Mathews and Dewey [115] found that ultraviolet light accelerates the rate of sodium sulfite oxidation and demonstrated that stoichiometrically the thermal and photochemical reactions are identical. Later, Mathews and Weeks [116] studied the effect of different organic compounds on the rate of photochemical sulfite oxidation. The esters, pyridine, phenol, hydroquinone, benzaldehyde and other substances were all found to retard the oxidation, although their efficiency as inhibitors varied markedly. Copper sulfate, which, according to Titoff, is a strong catalyst of the thermal reaction, was found to have no effect on the rate of the photochemical reaction. More recently Mason and Mathews [117] affirmed that copper sulfate is a strong inhibitor of the light reaction. Unfortunately not much weight can be attributed to this new evidence, since their other experimental results also differ from those of Mathews and Weeks. Mason and Mathews nevertheless give no reasons for the true cause of these divergencies.

The chain character of the photochemical oxidation of sodium sulfite was demonstrated by Bäckström,[118] since he found as many as 50,000 molecules react per absorbed quantum of wave length 2536 Å.

Alcohols affect the rates of photochemical and thermal reactions identically, according to Bäckström. The relative rates in presence of these inhibitors are satisfactorily represented in both cases by the equation

$$V = \frac{k_1}{k_2 c + k_3}$$

where c is the concentration of the inhibitor and the constants k_2

[115] *J. Phys. Chem.*, 17, 211 (1913).
[116] *J. Am. Chem. Soc.*, 39, 635 (1917).
[117] *J. Phys. Chem.*, 30, 414 (1926).
[118] *J. Am. Chem. Soc.*, 49, 1460 (1927).

and k_3 have values common for both thermal and photochemical reactions.

Attracted by Christiansen's theory [119] Bäckström interprets his observations to mean that not only the photochemical but also the thermal oxidation of sodium sulfite is a chain reaction. The effect of inhibitors can then be reduced principally to an influence on the length of the chains; and, in so far as the thermal and photochemical reactions have the same secondary mechanism, it might have been expected that the inhibitors present would exert an identical retarding action on both of them. However the quantitative inhibitive action is not always the same for the two reactions. Bäckström observed for instance that hydroquinone is a more powerful inhibitor of the light reaction, at least in light of the wave length 2536 Å. He relates this effect with its known absorption spectrum,[120] suggesting that in photochemical oxidation of sodium sulfite the "normal" inhibiting action of hydroquinone is possibly intensified by its absorption of active radiation, that is, by its acting simultaneously as an inner light filter. The presence of the constant k_3 in the above equation indicates furthermore, according to Bäckström, that besides the added inhibitor, some other and independent cause must limit the length of the thermal or photochemical chains.

Oxidation of Aldehydes. The experiments of Bäckström on the photochemical oxidations of benzaldehyde and oenanthaldehyde revealed that these reactions, like that of sodium sulfite, must have a chain mechanism. About 10,000 molecules of benzaldehyde react per quantum of absorbed light energy, the yield being approximately constant in the region 3660-2536 Å. The quantum yield of oenanthaldehyde oxidation increases from about 7500 in light of the wave length 3130 Å. to about 15,000 molecules per quantum in the light 2536 Å.

Here, too, it was shown qualitatively that all substances which retard the photochemical rate of reaction act analogously in the thermal reaction. Quantitatively, however, the relations are not as simple as in the case of sulfite oxidation. The following substances, for instance, inhibit the photochemical oxidation of benzaldehyde less strongly than they do the thermal reaction: diphenylamine, phenol, anthracene and trichloracetic acid. In these cases as well, Bäckström raises the question as to whether or not these substances act simultaneously as inner light filters, since they actually absorb ultraviolet radiation of those wave lengths which he was using in his

[119] *J. Phys. Chem.*, 28, 145 (1924).
[120] Wright, *J. Chem. Soc.*, 103, 528 (1913).

experiments. He comes, however, to the conclusion that such action does not play an important rôle in the reaction mechanism. The inhibitive action by picric acid and α and β napthols on the photochemical oxidation of oenenthaldehyde can be satisfactorily expressed by an equation of a form similar to that obtained with sulfite solutions:

$$V = \frac{k_1}{k_2 c + k_3}$$

The constants k_2 and k_3 of this equation were found by Bäckström to be independent of the wave length of incidental monochromatic radiation, varied from 3660 to 2536 Å., although the light absorption coefficients of these substances differ very markedly. The rate of the thermal oxidation of oenanthaldehyde follows a different law, being inversely proportional (i.e., the constant k_3 is now zero) to the concentrations of the same inhibitors.

For a long time it has been generally accepted [121] that autoxidations proceed in two stages: the primary reaction between oxygen and the autoxidisable substance leads to the formation of a more or less unstable peroxide; the subsequent reaction between the latter and a non-oxidised molecule results in the formation of the final oxidation product. It has been mentioned above that Moureu and Dufraisse employed this interpretation in explaining inhibitor action. Quite recently Bäckström [122] carried out an investigation from this point of view on the photochemical autoxidations discussed above and obtained results of considerable importance for a complete elucidation of their reaction mechanism. He found that just as in the thermal oxidation of benz- and oenanth-aldehydes, so also in their photochemical reaction with oxygen, the primary process is the formation of a peracid molecule, which then reacts with another aldehyde molecule. The quantum yield of the peracid formation was found to be very large; in fact so large that it is mainly to the long chain reaction of this first stage that Bäckström attributes the chain character which he observed for the completed autoxidations. The secondary reaction of the peracid with aldehyde, for instance:

$$C_6H_5CO_3H + C_6H_5CHO \rightarrow 2C_6H_5COOH$$

is also light sensitive but the quantum yield is much smaller. According to Bäckström's estimates it varies in his experiments from 2 to 18, suggesting that, in this reaction as well, chains, although they are

[121] Comp. Engler and Weissberg, "Kritische Studien über die Vorgänge der Autoxydation"; Braunschweig, 1904.
[122] *Meddel. Vet. Akad. Nobelinstitut*, 6, No. 15 (1927).

rather short, are started on absorption of light energy quanta. The rate of the dark reaction of the benzoperacid with benzaldehyde can be measured at room temperature. This reaction has been found to be unimolecular with respect to the peracid and at 20° C. to be half completed in somewhat less than 30 minutes.

In the light of these experiments, Bäckström pointed out that some of his other observations on the reaction rate in light and dark obtain a relevant interpretation. Thus, he found that the rate of the photochemical oxidation of benzaldehyde decreases rapidly on prolonged illumination; on the other hand, the thermal reaction is faster after an illumination than before. Both these effects are due to the photochemical formation of the peracid. The first effect is caused by an increase in concentration of the peracid [123] since an increasing fraction of activated aldehyde molecules react in the following manner:

$$C_6H_5CO_3H + C_6H_5CHO \rightarrow 2C_6H_5COOH$$

instead of by:

$$C_6H_5CHO + O_2 \rightarrow C_6H_5CO_3H;$$

and since the length of chains in the former reaction is relatively much shorter, in other words since the reaction leads less frequently to the formation of activated molecules, the total rate slows down. On the other hand, the accumulation of larger quantities of peracid during illumination may increase the rate of the thermal reaction between aldehyde and oxygen and thus cause a photochemical after effect, since, according to Bäckström, chains may be started by the thermal reaction between peracid and aldehyde, as well as by the photochemical reaction.

Another effect observed by Bäckström remains unexplained, but unfortunately it was not investigated more in detail: the quantum yields of the formation and of destruction of the peracid are dependent on the light intensity; in other words the reaction rate is not proportional to the incident light intensity. This phenomenon likewise appears in the oxidation of the hydriodic acid, to be discussed below, and possibly constitutes one of the kinetic features of all photochemical autoxidations.

Bäckström succeeded in demonstrating that all three autoxidations investigated by him can be photosensitised to longer waves by adding various light-absorbing substances. Thus, for instance,

[123] Bäckström estimates that in his experiments the concentration of the peracid on illumination became many times greater than the concentration of the dissolved oxygen.

diacetyl and benzil act as photosensitisers for benzaldehyde oxidation; benzophenone, benzil, benzaldehyde, etc., in the reaction of oenanthaldehyde; sodium benzoate, sodium salicylate, acetone, rhodamine B, potassium iodide, etc., in the oxidation of sodium sulfite solutions. His experimental results are not quite simple; for instance the sensitisers for the oxidation of oenanthaldehyde, with the exception of benzophenone, decrease the reaction rate in varying ratios in light of those (shorter) wave lengths which are absorbed by aldehyde itself. On the other hand, sodium benzoate and potassium iodide increase manyfold the rate of oxidation of sodium sulfite in light of the wave length 2536 Å.; undoubtedly this action is not due to an increased absorption of light, but, as Bäckström concludes, is either due to a more efficient utilisation of the absorbed light energy by the photosensitiser or to the sensitiser itself taking an active part in the chain mechanism in addition to acting in its first capacity.

The mechanism of these photosensitisations is probably not a direct transfer of energy on inelastic collisions. Bäckström finds that the process by which the reaction chains are started in the photosensitised peracid formation is probably a photochemical reaction between the sensitiser and oxygen. Such a mechanism is more than probable in a case like the photosensitisation of the oenanthaldehyde oxidation by benzaldehyde [124] and is furthermore supported in the case of sulfite oxidation by experiments of Noak,[125] who found that this reaction can be photosensitised to visible light by means of eosin, fluorescein and methylene blue and that peroxides of the sensitisers are formed intermediarily.

In discussing the mechanism of the reaction chains Bäckström [126] specified the original theory of Christiansen by suggesting that the "hot" molecules of the reaction products transfer their energy to the molecules of the reactant, causing them to be excited into those quantum states which are responsible for their ultraviolet absorption spectra. This concept of the links in the chains enables Bäckström to explain why some of the thermal autoxidations have side reactions otherwise caused only by ultraviolet light; why some of these reactions show the phenomenon of chemiluminescence to a very marked degree; and finally to relate their unusual features to their very high heats of reaction. His view on the nature of the links in the reaction mechanism of the thermal and photochemical chains is very similar

[124] It is interesting to note that Mathews and Weeks (*loc. cit.*) observed that benzaldehyde acts as a strong inhibitor of the photochemical oxidation of sulfite solutions.
[125] *Z. Botanik*, 12, 273 (1920).
[126] *Meddel. Vet. Akad. Nobelinstitut*, 6, No. 16 (1927).

to the theory of the chains in the photochemical hydrogen chlorine reaction postulated originally by Bodenstein (see page 88).

Oxidation of Hydrogen Iodide. A great deal of experimental work was carried out on the photochemical oxidation of hydrogen iodide in aqueous solutions, but the results are contradictory and their interpretation very incomplete. The first quantitative study of this reaction was undertaken by Plotnikoff,[127] who found that the oxidation of acid solutions of potassium iodide, which proceeds at a measurable rate in the dark, is markedly accelerated by light of the spectral region around 4360 Å. Plotnikoff claimed that this narrow spectral region alone is photochemically active. His study on the influence of different reactants led him to the conclusion that the velocity of photochemical oxidation was proportional to the concentration of dissolved oxygen, but increased less rapidly than the iodide or hydrogen ion concentrations. He also found that the rate was proportional to the incident light intensity and, assuming this relation to hold strictly, demonstrated that the photochemical reaction rate was not influenced by the velocity of the simultaneous thermal oxidation. In other words, he concluded that both reactions follow the so-called additivity rule [128] of thermal and photochemical reactions. The mechanism was further elucidated by experiments of Strachoff,[129] represented in the following Table 30, and showing the effect of iodine on the photochemical oxidation of hydriodic acid. The iodine was used (1) as a separate light filter, (2) in the reacting solution which was made 0.1 normal with respect to potassium iodide and hydrochloric acid.

TABLE 30.

Monochromatic light 4360 Å.

1. Iodine as light filter (2 cm. layer)

I_2 millimols per liter	0.0	2.0	3.0	8.0	16.0	25.6	
Rate of reaction..	120	105	80	60	16	8	(the rate of thermal oxidation)

2. Iodine in the reacting solution (2.5 cm. layer)

I_2 millimols per liter	0.0	2.7	12.3	27.0	53.4	61.3	67.9	87.0	134.6
Rate of reaction..	120	120	120	119	80	72	60	50	45

According to Strachoff, the marked difference between these two sets of experiments indicates that the ions I_3^-, in which form the iodine is mainly present,[130] have a specific accelerating influence, probably by

[127] *Z. physik. Chem.*, 58, 214 (1907); 64, 215 (1908).
[128] Plotnikoff. "Lehrbuch der Photochemie." 1921.
[129] *Z. wiss. Phot.*, 18, 227 (1919).
[130] For the determination of the equilibrium $I_2 + I \rightleftarrows I_3$; comp. Fedotieff, *Z. anorg. Chem.*, 69, 91 (1911).

photosensitisation, on the rate of reaction. They thus partly compensate their own retarding inner filter action. His views were confirmed by Winther,[131] who even concluded that solutions of hydriodic acid free from iodine are non-sensitive to light. Winther thus attributed the photochemical oxidation entirely to the primary absorption of light by the I_3^- ions which are present. In a more recent paper [132] he substantiated his claims by showing that absorption of light by the iodide ion, I^-, becomes marked only below *circa* 2600 Å. At the same time, he presented new measurements which disagreed with those of Plotnikoff on the rate of hydriodic acid oxidation. Winther considered that the earlier investigations had established that the triodide ion I_3^- is the light absorbing component and thus the origin of photochemical oxidation. Consequently, he worked throughout with solutions of acidified potassium iodide containing definite amounts of iodine, usually large enough to ensure a complete light absorption in the spectral region employed, 4360-2500 Å., which was found to be active photochemically throughout. The experiments, carried out mainly in monochromatic light 3660 Å., showed that the reaction velocity is not proportional to the incident light intensity. Winther's data indicate that, at low light intensities (50-400 ergs per sec.), the rate of oxidation is approximately proportional to the square root of the intensity, whereas, at higher light intensities, it passes through a maximum or reaches a steady maximum value, since a doubling (780 to 1600 ergs per second) of the absorbed light energy beyond that point results in only a 10 per cent decrease in the oxidation velocity. Furthermore, although, in a general way, Winther confirmed Plotnikoff's observations that the rate of oxidation was dependent on the concentration of potassium iodide, hydrochloric acid, and oxygen, and independent of the amount of iodine present unless the light absorption by the I_3^- ions is incomplete, the details of the former's observations are found to differ markedly from that of the latter's. Thus, for instance, Winther found that the reaction velocity was proportional to only the ¾ power of the oxygen concentration, and that the effect of varying the potassium iodide concentration was negligible when the latter was above about 1.0 normal. Winther's measurements of the absorbed light energy enabled him to calculate the quantum yield in the hydriodic acid oxidation. He, of course, obtained varying yields, some of those found under the most favourable conditions, i.e., low light intensity, high concentrations of the reactants,

[131] *Kon. Danske, Vid. Selsk. Mat. phys. Medd.*, 2 No. 2 and 3 (1920).
[132] *Z. physik. Chem.*, 108, 236 (1924).

being more than a hundred iodide ions oxidised per quantum. Under otherwise identical conditions, the yield was found to be more or less independent of the wave length of the absorbed radiation, which varied in different experiments from 4360 to 2536 Å.

As an explanation for these kinetic relations, Winther advanced a theory in which he assumed that the I_3^- ions, the primary cause of photochemical oxidation of hydriodic acid, are activated upon quantised absorption of light energy; and that while they are still in the excited state they are capable of absorbing further energy quanta. Only those ions, however, which have absorbed one quantum can cause the photochemical reaction; whereas, by the absorption of subsequent quanta, they become deactivated in so far as their photochemical action is concerned. It is obvious that, qualitatively, this theory accounts for the decrease of the quantum yield observed upon increasing the light intensity, since the chance is thereby increased that an activated I_3^- ion before it can be consumed in the photochemical process may absorb a second light energy quantum. Winther justified this qualitative statement by quantitative calculations. The actual chain mechanism of the photochemical reaction involves, according to Winther, the re-emission of a part of the absorbed radiation as a fluorescence of short wave length by each I_3^- ion which has absorbed only one energy quantum; the absorption of this secondary radiation by the reactants O_2, etc., and eventually the renewed emission of light by the reactants.

This theory of Winther's was previously discussed on page 156 and its complete disagreement with the results of modern physical investigations, in particular with the Stokes rule of fluorescence, has been mentioned. Furthermore, Winther's assumption of "many quanta absorption" forces him to introduce extraordinarily large absorption coefficients and "lives" of activated molecules, unsupported by other experiments. For instance, in order to obtain an agreement between theory and experiment, he deduces that, at his highest light intensity (only 320 ergs per cm^2., per second), approximately 88 per cent of all the tri-iodide ions absorb the second quantum before they can re-emit the first one. These values are a sufficient indication of the impossibility of reconciling Winther's theory with the usual data on the behaviour of excited molecules. Besides, this theory does not necessarily follow from his experimental data. Even accepting them without reserve, the inherent difficulty of Winther's explanation may be avoided by making a different, less unlikely, assumption: namely, that, in the chain mechanism, one of the links is a relatively slow

thermal process which determines the rate of the total reaction when, due to higher light intensity, the rates of other processes involved are relatively large. This assumption will, of course, explain Winther's observations that the rate of photochemical reaction cannot rise above a certain maximum value even if the light intensity is further increased. However, a more detailed kinetic discussion is rather premature, due to considerable divergencies in the results obtained by Plotnikoff and by Winther. Unfortunately, both of these investigators were somewhat handicapped by the circumstance that the photochemical reaction superposes a thermal one which, in the latter's experiments, for instance, amounted to more than 50 per cent of the total rate. Both investigators arrived at a value for the rate of photochemical reaction through the usual way of calculating the rate of thermal reaction for the conditions of the light experiment and of subtracting this value from the measured total rate. While this method of determining the rate of photochemical reaction is perfectly justifiable as long as the change due to thermal reaction is but a small fraction of the total change, very noticeable systematic errors in the final values may result from an inaccurate determination of the order of the thermal reaction in a case like the oxidation of hydriodic acid. Finally, this method of calculation contains the implicit assumption that the rate of neither thermal nor photochemical oxidation is influenced by their simultaneous occurrence; in other words that they follow the additivity rule of Plotnikoff. That the latter attempted to support his rule by experiments has already been mentioned. However, his experimental evidence is valueless, since the basis of his experiments—an assumed proportionality between the rate of photochemical oxidation of hydriodic acid and the light intensity—was discredited by more recent investigators.

In discussing Winther's experimental results, Berthoud [133] suggested that they may be partially complicated by some unknown source of errors, and that the real relation between the velocity of hydriodic acid oxidation in presence of iodine and the light intensity is one of square root proportionality. Drawing a parallel with other reactions of iodine, Berthoud concluded that, in the oxidation of hydriodic acid as well as in the reaction of iodine with potassium oxalate, the primary products formed upon light absorption, causing subsequent chain reaction, are iodine atoms. He also pointed out that the retardation of the reaction rate by large amounts of iodine as observed by Strachoff is identical with effects observed and interpreted by him

[133] *Trans. Farad. Soc.*, 21, 554 (1925).

for the iodine-potassium oxalate reaction. A confirmation of Berthoud's suggestion would open up a point of attack for the study of the secondary reactions in the hydriodic acid oxidation. It must be remarked, however, that, according to Berthoud, not the tri-iodide ion I_3^- but only the molecule I_2 is dissociated into atoms upon light absorption. Consequently, the real quantum yield of Winther's experiments, calculated now for the light energy absorbed by only the molecule, is considerably greater than his values given above, inasmuch as the concentration of the iodine molecules in solution is governed by the relation [134]

$$\frac{[I_2] \cdot [I^-]}{[I_3^-]} = 0.0012 \text{ (at } 20°)$$

and the light absorption coefficients of the ion I_3^- and the molecule I_2 are of the same order of magnitude. Furthermore, although this equilibrium relation indicates that an increase of iodide ion concentration should decrease the rate of reaction, the reverse was observed by Plotnikoff and by Winther. On closer consideration, even the experiments of Strachoff disagree somewhat with Berthoud's theory. Thus, in the former's experiment (Table 30, page 201, with a solution 0.087 *M* with respect to iodine, the ratio I_2/I_3^- is about 1:13; in the experiment following that (0.134 *M* I_2) the ratio I_2/I_3^- is 1:3; but the rate of reaction actually has decreased (from 50 units in the former to 45 units in the latter). Berthoud's theory is therefore not in a complete agreement with the present experimental data.

We have discussed so far the action of light on acidified solutions of potassium iodide. Ross [135] and Kailan [136] found that ultraviolet light causes a slow decomposition also of the neutral solutions of different salts of hydriodic acid. The results of these investigations, however, offer little material for kinetic study.

Pinnow,[137] Viale [138] and others examined the effect of various foreign substances on the rate of reaction in acidified and neutral solutions of iodides. Apparently, under certain conditions of acidity, quinine and some dyes act as photosensitisers of the reaction, but the experimental evidence is not very conclusive. With the exception of the hydrogen ion concentration, and some experiments indicated by Pinnow [139] and by Plotnikoff,[140] little systematic investigation has

[134] Fedotieff, *loc. cit.*
[135] *J. Am. Chem. Soc.*, 28, 786 (1906).
[136] *Monat. Chem.*, 34, 1209 (1913).
[137] *Ber.*, 34, 2528 (1901).
[138] *Atti acad. Lincei*, 31, II (1920), and other publications.
[139] *Loc. cit.*
[140] *Loc. cit.*

been carried out on the influence of other ions on the rate of hydriodic acid oxidation.

Oxidation of Iodoform. Catalytic phenomena of a somewhat different nature were reported by investigators on the photochemical reaction of iodoform. Hardy and Willcoc,[141] who carried out the first detailed study of this reaction, found that solutions of iodoform in chloroform or benzene containing dissolved oxygen are oxidised to iodine by the action of light. They confirmed earlier observations, that solutions of iodoform were perfectly stable in the dark at room temperature, but decomposed slowly once the oxidation has been initiated by illumination. In other words, iodoform solutions exhibit "photochemical after-effects." The quantitative determination of the reaction products was carried out by Schoorl and van der Berg,[142] who showed that two simultaneous reactions occur. They affirm that about 80 per cent of the iodoform is oxidised according to the stoichiometric equation

$$2CHI_3 + 3/2\,O_2 = 2CO + H_2O + 6I$$

and the rest according to the equation

$$2CHI_3 + 5/2\,O_2 = 2CO_2 + H_2O + 6I,$$

and they suggest that the first reaction actually proceeds in steps, thus:

(1) $CHI_3 + O = COI_2 + HI$; (2) $COI_2 = CO + I_2$; (3) $2HI + O = H_2O + I_2$.

Bela Szilard,[143] studying the kinetics of iodoform oxidation, came to the conclusion that the rate is approximately unimolecular but that the decomposition is incomplete. Additional experiments showed that this incompleteness is probably due to the retarding inner filter action of the iodine formed and that by removing this latter the reaction rate is accelerated. However, it is possible that another factor influenced Bela Szilard's experiments, namely, a varying concentration of dissolved oxygen which was kept high by frequent shaking of the reaction flasks only in those experiments in which iodine was removed by action of mercury.

The rate of decomposition of iodoform,[144] in the dark after an illumination, was found to decrease with time and usually to stop entirely before all the iodoform had been oxidised. This decay of

[141] *Proc. Roy. Soc.*, 72, 200 (1903); *Z. physik. Chem.*, 47, 347 (1904).
[142] *Ber. deutsch physik. Ges.*, 385 (1905).
[143] *Z. wiss. Phot.*, 4, 127 (1906).
[144] Actually the rate of formation of free iodine, since only this latter was estimated in the experiments of Bela Szilard and in those of Plotnikoff.

catalytic activity is approximately unimolecular and Bela Szilard compares it with the decrease of activity of enzymes.

Plotnikoff [145] found that the rate of the after-reaction was dependent on the concentration of iodoform in benzene, increasing as its 1.3 power; and that it had the relatively high temperature coefficient 2.6 in contrast to the small temperature coefficient 1.4 of the photochemical oxidation. Plotnikoff [146] was the first investigator to study systematically the effect of different solvents on the kinetics of iodoform oxidation. In the following Table 31 are given the relative values of the velocity constants of the photochemical iodoform oxidation in different solvents under otherwise identical conditions, the velocities of the after-reaction, and the light absorption coefficients ε of iodoform solutions for the wave length 4360 Å., which, separated by means of light filters, was used by Plotnikoff for the illumination of the reacting solutions.

TABLE 31. $\lambda = 4360$ Å.; $T = 20°$; $CHI_3 = 0.02$ *M*.

Solvent	Velocity constant	After-effect	ε	*D* Dielectric constant
CCl_4	39.4	2.4	23.4	2.2
C_6H_6	34.6	5.5	21.5	2.2
CS_2	24.1	—	45.9	2.6
$C_2H_5OC_2H_5$	16 (rapid autocatalytic increase)	—	10.9	4.3
$CH_3COOC_2H_5$	8.1	0.9	67.5	6.1
CH_3OH	3.2 (decrease of the constant; decomp. incomplete)	—	66.4	31.0
C_2H_5OH	2.5	—	10.2	26.0
CH_3COCH_3	0.7	—	53.0	21.5
$C_2H_5OH + 5\%\ H_2O$	1.4	—	—	—
$C_2H_5OH + 14.5\%\ H_2O$	0.7	—	—	—
$C_2H_5OH + 20\%\ H_2O$	0.5	—	9.7	33.5
$C_6H_6 + C_2H_5OH$	autocatalytic increase	—	—	—

The velocity constants of the second column were calculated by Plotnikoff by assuming that the amount of iodine formed increases linearly with time of illumination and that the rates of photochemical and of after-reactions follow the "additivity rule." The rates of the photochemical reaction, therefore, were obtained by subtracting the rate of the after-effect determined by special measurements from the total observed rate.

At first glance, the table offers an extraordinary variety of phenomena without suggesting interpretation. Plotnikoff pointed out that the variations of the reaction velocity and of the light absorption

[145] *Z. physik. Chem.*, 75, 337 (1910).
[146] *Ibid.*, 75, 337, 385 (1910); 76, 743 (1911).

coefficients in different solvents can hardly be correlated. Thus, the conclusion must be drawn that the different rate with which iodoform is oxidised in different solvents is not due to variations in the amount of light energy absorbed. Besides, under Plotnikoff's experimental conditions, practically equal amounts of light energy were absorbed in all the solvents used, the light absorption by a 0.02 molal solution of iodoform being complete. Although he stressed this conclusion, Plotnikoff considered a further discussion of the actual cause of the solvent catalysis premature. For a long time the problem was neglected until, recently, Winther [147] pointed out that in Plotnikoff's experiments the rate of iodoform oxidation decreases in the measure in which the dielectric constant of the solvent increases. The fifth column of the table, where these constants are reproduced,[148] shows that Winther's suggestion is on the whole supported by the experimental data, although there are a few exceptions, for instance, ethyl alcohol and acetone.[149] The data in the table indicate that the photochemical after-effect is undoubtedly also a function of the chemical composition of the solvent and that there is evidently no proportionality between the rates of photochemical and after-reactions in different solvents. Finally, as shown in Plotnikoff's experiments, the solvent influences the kinetics of the photochemical reaction to a very marked degree. Whereas, in the majority of the pure solvents and in the mixtures of ethyl alcohol and water, the amount of iodine formed increases linearly with time of illumination, the reaction thus being one of zero order, in ether and in mixtures of benzene and ethyl alcohol Plotnikoff finds a pronounced autocatalytic reaction; while, in methyl alcohol, the rate decreases rapidly to zero before all the iodoform has been oxidised. It is certainly astonishing that Plotnikoff finds a zero order reaction rate in several solvents, even when one of the reaction products—the iodine—which has a higher light absorption coefficient for the wave length 4360 Å. than iodoform, is acting as an inner filter and should retard the rate. It is rather improbable that the inner filter action of iodine should be balanced by the simultaneous production of that catalyst which causes the after-effect and additional iodine formation. Discussing the absence of iodine action, Plotnikoff pointed out that he had observed the same phenomenon in the oxidation of hydriodic acid. We know, however, that, in reality, iodine is

[147] *Trans. Farad. Soc.*, 21, 595 (1925).
[148] Landolt-Börnstein, "Physikalisch-chemische Tabellen."
[149] Winther's conclusion that the rate of anthracene polymerisation shows an analogous relation to the dielectric constant of the solvents is more doubtful, since, in reducing the reaction rate in different solvents to the same temperature, he used an incorrect value for the temperature coefficient of this reaction.

a photosensitiser of the hydriodic acid oxidation. It is possible that in the oxidation of iodoform iodine plays a similar rôle. The study of absorption spectra of iodine in different organic solvents [150] revealed with certainty the existence of complexes formed by iodine and solvent molecules, and possessing distinctive absorption spectra. It is not excluded that the formation of these compounds and their different photosensitising action on iodoform are contributing to the complexity of the observed phenomena. Another factor which probably influences the rate of iodoform oxidation is the unequal solubility of oxygen in the solvents used. This factor is possibly one of major importance, since earlier investigators found the reaction rate to be influenced by the oxygen concentration. However, all of these suggestions are only of a tentative character since Plotnikoff's data are too incomplete for a theory to be advanced and tested. The more recent investigations of Comanducci and Meduri [151] and of Butler [152] contribute on the whole very little material of theoretical importance. It is interesting to note that a comparison between the rate of iodine formation in Plotnikoff's experiments and a roughly calculated amount of light energy absorbed in these experiments indicates that the oxidation of iodoform proceeds, probably in all solvents, at a rate of more than one molecule decomposed per quantum of light energy absorbed and must therefore be a chain reaction.

Before concluding this chapter, the photochemical oxidation of complicated organic molecules, in particular, of certain dyes by free oxygen, will be briefly discussed. These oxidations are of great technical importance inasmuch as they constitute one of the main causes of the bleaching of dyes by light. Very little quantitative investigation, however, has been carried out on the subject. In this chapter it is impossible to enter into a discussion of the technically important problem of the influence which is exerted by the chemical constitution and by structure of the dyed material (threads) on the photochemical stability of the applied dyes. The study of this phenomenon has scarcely advanced beyond the stage of collecting bare facts. Our program will be limited to the discussion of a group of reactions in solution and of some of the phenomena observed in thin dyed films of collodion.

Oxidation of Quinine. A very interesting counterpart to the oxidation in light of quinine by chromic acid is its photo-oxidation by free

[150] Plotnikoff, *loc. cit.*
Stobbe and Schmitt, *Z. wiss. Phot.*, 20, 57 (1920).
[151] *Gazz. chim. ital.*, 48, I, 238 (1918).
[152] *Chem. News*. 125. 38 (1922).

oxygen, studied in detail by Weigert.[153] He found that oxygen is absorbed by aqueous quinine solutions under the action of the violet and near ultraviolet lines of the mercury spectrum, and that, in this reaction, as in that with chromic acid, the quinine molecules are the light absorbing component. In other respects, however, this reaction is extraordinarily unlike the one earlier discussed. The rate of oxygen consumption is markedly retarded by the hydrogen ions and an acid

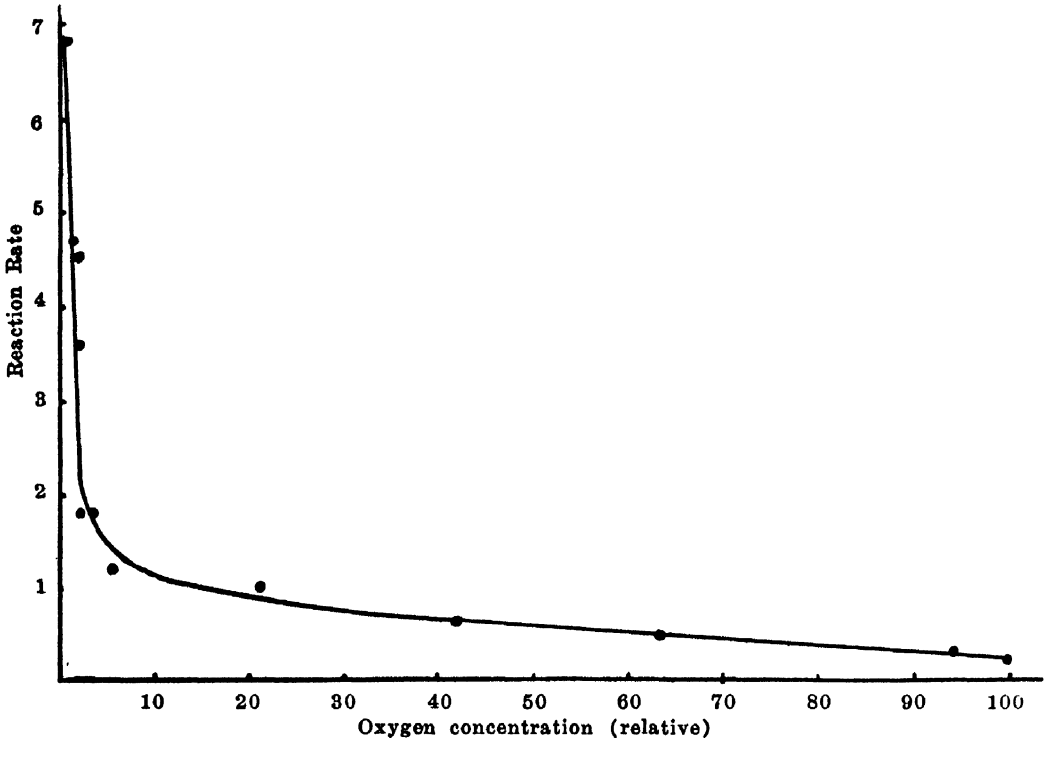


FIGURE 6.—The Rate of Oxidation of Quinine by Oxygen.

concentration (HCl) of 0.1 normal is sufficient, according to Weigert, to bring the reaction to a complete standstill. Unusual is the effect of oxygen, which, although itself a reactant, was found to retard the rate to a very marked degree. The reaction was studied by Weigert in solutions satuated by nitrogen-oxygen mixtures of varying composition but of identical total pressure. Results obtained under these experimental conditions are represented in Figure 6 where the relative rate of quinine oxidation is plotted against percentage oxygen concentration. The relation is almost exactly one of reverse proportionality. Weigert pointed out, however, that undoubtedly an optimum oxygen concentration must exist, since in its complete absence

[153] *Nernst-Festschrift*, Halle a.S. (1912).

the reaction rate is equal to zero. Experiments with systems containing initially very small amounts of oxygen confirm his conclusion, since the rate of quinine oxidation upon prolonged illumination passes through a maximum (the "optimum concentration") and then rapidly decreases to zero. At this point the consumption of oxygen is almost complete.

As was shown by Weigert, the retardation by oxygen is not due to the formation of a stable inhibitor, because freshly prepared solutions of quinine show the same reactivity as any other solutions of the same oxygen content, even though the latter may have been prepared by illuminating quinine solutions containing originally excess oxygen. On the other hand, the reaction undoubtedly proceeds through the formation of stable intermediary products of peroxide character. This is evidenced by earlier experiments of Jodlblauer and Tappeiner [154] who discovered that previously illuminated quinine solutions oxidise iodide ion. Their observation was confirmed by Weigert, who further concluded, on the basis of rather uncertain colorimetric determinations, that the active oxygen is not present as hydrogen peroxide, but is probably associated with quinine molecules. This peroxide is undoubtedly not a by-product, but one of the intermediary stages of the main reaction, since Weigert could obtain as much as 42.5 per cent of chemically absorbed oxygen in the "active state." The yield of peroxide relatively to the amount of oxygen consumed was found to decrease with partial pressure of oxygen. Its absolute amount, however, formed under otherwise identical conditions, was practically independent of the concentration of oxygen. Weigert discovered furthermore that, although the peroxide is stable in the dark at room temperature, it is decomposed by the action of the same wave length which causes the oxidation of quinine. This last observation is particularly important, since it shows the obviously intermediary character of peroxide formation, although of course it offers as yet no explanation as to why oxygen retards the reaction. The quantum sensitivity of the quinine oxidation by free oxygen is very low in contrast to its oxidation by chromic acid. Bodenstein [155] estimated that, even under favourable conditions as many as 200 light quanta are absorbed by quinine per reacting oxygen molecule.

Oxidation of Dyes in Solution. In connection with this study of quinine oxidation, Weigert demonstrated that the phenomenon of inhibition by oxygen is likewise common to some other photochemical

[154] *Münchener medizin. Wochenschr.*, 1139 (1904).
[155] *Z. physik. Chem.*, 5, 356 (1913).

oxidations in aqueous solutions, namely to those of fluorescein and of tetraiodofluorescein. It is in fact very probable that it will be found that other dyes of the fluorescein type behave similarly. The photochemical destruction of dyes, especially of this particular chemical group, aroused considerable interest since Perrin [156] attempted to link their sensitivity to light with their ability to fluoresce. His original theory suggested that the activated molecules, formed upon absorption of light quanta, undergo a chemical change accompanied by a simultaneous emission of the excess energy in the form of fluorescence radiation. Now, according to the quantum theory, the frequency of emitted radiation is determined by the energy content of the molecule before and after the process of light emission. If, therefore, a photochemical reaction, which necessarily involves a change in quantum levels of the reacting molecule, is accompanied by fluorescence, the wave length of the emitted light must necessarily be different from the light absorbed by the original molecule. This theory, indicating the cause of the non-resonance character of the emission of fluorescence light by dye solutions, predicted a complete parallelism of the effects of different physical and chemical factors on the rate of their photochemical destruction and on the intensity of fluorescence. The difficulty of the theory becomes evident when it is considered that certain dye solutions exposed to daylight retain their fluorescence apparently unchanged for years, although the total number of absorbed and emitted light energy quanta by far exceeds the number of fluorescent molecules present. In addition to this, Wood [157] and Pringsheim [158] have demonstrated that the rate of photochemical destruction does not always run parallel with the intensity of fluorescence; in fact they may even oppose each other. Thus, for example, eosin and fluorescein show a much more brilliant fluorescence in alcoholic solutions even though the rate of their destruction by light is faster in aqueous solutions. Again, while the temperature coefficient of the intensity of fluorescence is practically equal to unity, the photochemical reaction can be brought to a complete standstill by decreasing the temperature to —190°. Wood and Pringsheim also discovered that, whereas the fluorescence is proportional to light intensity, the photochemical reaction is favoured by high densities of incident radiation. These experiments were carried out in such a way that the same total amount of light energy was either distributed in the whole vessel containing the fluorescent solution, or was concentrated upon a small

[156] *Ann. Physique*, 10, 133 (1918).
[157] *Phil. Mag.*, 43, 757 (1922).
[158] *Z. Physik*, 10, 176 (1922); 16, 71 (1923).

portion of it. In the first case, the solution remained unchanged, whereas in the second the dye present was completely destroyed to the extent to which it diffused into the illuminated part of the solution. From all of these observations, Pringsheim concluded that the destruction and fluorescence of molecules are two independent phenomena. Activated molecules formed upon light absorption either emit the excess energy as fluorescence light or undergo a chemical reaction. He suggested that, since this last process is favoured by a high density of radiation, it is probable that those molecules react which absorbed a second light energy quantum before the first one can be re-emitted as fluorescence. Another plausible explanation for the acceleration of the chemical reaction by high light intensities is, in Pringsheim's opinion, the assumption that the process requires the collision of two activated molecules. The second mechanism is apparently more probable since Pringsheim showed that the chemical reaction takes place not only in polychromatic, but also in strictly monochromatic light. This excludes those molecules which might absorb a small and a large energy quantum. It would be necessary, therefore, in order to retain the first mechanism, to assume that molecules are capable of subsequent absorption of two identical quanta. Another interpretation of the processes in fluorescent dye solutions was advanced by Weigert,[159] who called attention to the fact that the oxidation of dyes is retarded by oxygen according to his own experiments. The relatively rapid reaction setting in in the intensely illuminated portion of the solution in the experiments of Wood and Pringsheim, must cause, according to Weigert, a decrease in the local oxygen concentration, the latter being supplied only by a slow process of diffusion. The rate of oxidation will thus be autocatalytically accelerated and the final result will be, in agreement with observations, a more rapid oxidation of the total amount of dye present in the solution and diffusing, like oxygen, into the illuminated part of it. Pringsheim believes that Weigert's theory is untenable, but his objections are not fully justified, inasmuch as a local decrease of oxygen concentration undoubtedly takes place under his own or Wood's experimental conditions, unless oxygen does not take part in the resulting reaction. This last point is uncertain since the chemical processes realised by Weigert and by Pringsheim in their experiments, and not investigated any further, may be chemically (and kinetically) quite different. The former employed neutral aqueous solutions of fluorescein, whereas the latter states that the presence of alkali and of alcohol (small quanti-

[159] *Z. Physik*, 10, 349 (1922).

ties) is a necessary condition for the reproduction of the effects of light observed by him. Pringsheim's description of the chemical processes taking place in illuminated dye solutions indicate their composite character. Thus, initially, a rapid reaction, manifested by a change in the colour of the solution and by an increase of fluorescence intensity, takes place. This reaction is then followed by a slower and complete decoloration of the solution and a simultaneous destruction of fluorescence. In which of these processes, if at all, oxygen is involved remains unknown since their chemical nature has not been investigated. The original theory advanced by Pringsheim assumed that the primarily formed activated fluorescent dye molecules either re-emit the absorbed light energy as radiation or react chemically. More recent investigations of Wawiloff [160] and of others demonstrated that the third process by which the activated molecules can lose their excess energy, namely by the degradation of energy through inelastic collisions, plays an important rôle in the energy balance of illuminated fluorescent dye solutions. This was made obvious by the discovery that, even when the photochemical reaction is practically excluded, the number of emitted light quanta equals the number of absorbed only under particularly favourable conditions.

Reactions of Dyes in Collodion Films. The action of light on certain dyes in the solid state, mainly in solid solutions in thin collodion films, was the object of extensive and repeated studies by Lasareff and his co-workers. Simple relations indicated by their earlier investigations have subsequently proved more complicated than originally assumed, but, nevertheless, these investigations retain the historical importance of being the first photochemical experiments in which the study of the influence of wave length of incident radiation on the rate of photochemical reaction was combined with exact measurements on absolute amounts of absorbed light energy. Originally, Lasareff [161] proposed that the rate of bleaching of different dyes in collodion films is determined solely by the amount of absorbed light energy and is independent of the wave length of incident radiation. The spectral region studied was between the limits 5400-6400 Å. and was thus rather narrow. The measurements of the absorbed light energy revealed that the amounts of energy required for the decomposition of different dyes exceeded by far even their heats of combustion. In Table 32 are given the numbers of calories of radiant energy which cause the decomposition of one gram of corresponding dye.

[160] *Z. Physik*, 22, 266 (1924); 31, 750 (1925).
[161] *Ann. Physik*, 24, 661 (1907).

TABLE 32.

Chinaldincyanin	16,000 cal/gram.
Pinachrom	30,000
Cyanin	48,000
Lepidincyanin	58,000
Pinaverdol	117,000

These values indicate, as Bodenstein [163] pointed out, that hundreds of light quanta must be absorbed in order to decompose one dye molecule. In a subsequent paper, Lasareff [163] showed that the rate of bleaching of cyanin and of orthochrom in solid films of pure dye and of pinacyanol in collodion films is dependent on the wave length of absorbed radiation. Thus, the photochemical yield per calorie absorbed decreased for cyanin in the ratio 1:0.44 between the wave lengths 5430 and 6320 Å., for orthochrom in the ratio 1:0.71 (5430-6040 Å.), and for pinacyanol in the ratio 1:0.39 (5360-6320Å.). Lasareff attempted to reconcile these results with his earlier observations by suggesting that the photochemical yield is independent of the wave length only within a single absorption band and can vary for different bands. In his opinion, the absorption spectrum of these more recently investigated dyes actually indicates the presence of several partly overlapping absorption bands in the spectral region examined and thus confirms the advanced theory. Recently, Lasareff [164] renewed his discussion on the influence of wave length on the rate of bleaching, and proposed again that, within a single absorption band, the rate is determined not by the number of absorbed quanta but, independently of the wave length, by the amount of absorbed light energy. His measurements, however, extend over an insufficiently wide spectral region to allow a definite conclusion, so that they satisfy both these possible relations equally well.

The chemical process involved in the bleaching of dyes is mainly their oxidation by oxygen, according to Lasareff.[165] He obtained further the following kinetic equation as the result of his studies of the influence of oxygen concentration in the gas phase surrounding the illuminated dyed collodion films on the rate of bleaching

$$-\frac{dc}{dt} = k_1 I_{abs.} (k_2 + 1 - e^{-k_3[O_2]}$$

This equation shows that the relation between oxygen pressure and the rate of reaction is linear as long as the former remains small, but

[162] *Z. physik. Chem.*, 85, 357 (1913).
[163] *Ann. Physik*, 37, 812 (1912).
[164] *Trans. Farad. Soc.*, 21, 475 (1925).
[165] *Z. physik. Chem.*, 78, 657 (1911); 98, 94 (1921).

that the rate of reaction becomes independent of oxygen concentration at very high pressures (a hundred atmospheres and more). Besides the reaction due to the presence of oxygen in the films, the light causes another chemical process, similarly manifested by decoloration, which proceeds unaltered even in complete vacuum. Its chemical nature is not established, but apparently nitrocellulose is involved, since Lasareff [166] found that pure dye films deposited from alcoholic solutions are not bleached by light in the absence of oxygen. The rate of bleaching in vacuo is, like that in presence of oxygen, dependent on the chemical constitution of the dye. Thus, lepidincyanin shows a much more rapid vacuum rate than cyanin and pinachrom. Lasareff interpreted the observed influence of oxygen pressure on the rate of reaction by suggesting that either the rate is strictly proportional to internal oxygen concentration in the collodion films and that this varies with external pressure as the expression $1 - e^{-k_a[O_2]}$, or that at higher external pressures the concentration of oxygen in the films is sufficiently great to enable all activated molecules, formed on light absorption, to undergo the process of oxidation. In such a case oxygen must lose its influence on the rate of reaction.

The temperature coefficient of the photochemical bleaching of dyes was studied by Schwezoff,[167] who obtained rather small values (ranging from 1.04 to 1.08) for different dyes in collodion films. In contrast to most of the determinations of temperature coefficients of photochemical reactions, in which a possible change of light absorption with temperature was neglected, those of Schwezow were made for the same amount of light energy absorbed at different temperatures. Slightly different and higher values would be obtained if the usual method were followed, since, according to Lasareff,[168] the light absorption coefficients of dyes in collodion films increase markedly with temperature, and this influence of temperature is particularly pronounced on the longer wave side of their absorption bands.

Wawiloff [169] studied the thermal bleaching of pinaverdol, cyanin, lepidincyanin and chinaldincyanin, all of which proceed at a measureable rate between 60° and 120° and are entirely due to the catalytic influence of collodion, since pure solid dyes are completely stable in this temperature interval. The kinetics of these thermal processes varied for different dyes and were rather complicated. Oxygen has only a small accelerating influence on the rate of bleaching. The

[166] "Bleaching of Dyes in Visible Light," Monograph, Moskau (1911); see also Worel in Eder's *Jahrb. Phot.*, 18, 42 (1904).
[167] *Z. wiss. Phot.*, 9, 65 (1910).
[168] *Z. physik. Chem.*, 100, 266 (1922).
[169] *Ibid.*, 88, 85 (1914).

rate, however, is autocatalytically accelerated by some (undetermined) gaseous products of the reaction. Furthermore, as in most other cases, the temperature coefficients of the thermal reactions were found to be much higher than those of the photochemical processes. They all range above 2.0 for 10° temperature change.

The very limited validity of those relations, which were formulated by Lasareff in the photochemical bleaching of dyes, was demonstrated recently by Weigert [170] and by Predwoditeleff and Netschajewa.[171] The latter found that the initial rate of bleaching upon illumination is proportional, *ceteris paribus*, to the absorbed light energy only at very small dye concentrations in the collodion films. With increasing dye concentration, the initial rate becomes its periodic function. This unusual effect of concentration still lacks complete interpretation. The authors suggest that the rate of bleaching is dependent not only on the state of single light absorbing molecules, but is also influenced by the electric forces exercised by the neighbouring dye molecules. This electric field may be responsible for the observed periodic phenomena, its influence being naturally felt only at high concentrations of the dyes. Weigert found that in the course of the photochemical reaction some inhibitors must be formed, since the rate of bleaching of previously illuminated dyed collodion films is much slower than the rate in unexposed films with an identical dye concentration. The action of these unknown inhibitors is not inner light filtering since the products of reaction are colourless. The experiments were carried out by Weigert in connection with his studies on the action of linearly polarised light on certain finely dispersed solid systems.[172] He found that, under certain conditions, such light may cause permanent dichroitic effects in silver chloride suspensions in gelatin or in collodion films dyed by cyanine and other dyes. Without entering into a detailed discussion of these complicated phenomena we will merely remark that Weigert postulates a mechanical displacement of molecules by a directed action of the electric vector of the electromagnetic radiation waves as their general cause.

[170] *Z. Physik*, 5, 410 (1921).
[171] *Ibid.*, 32, 226 (1925).
[172] *Verhandl. deutsch. phys. Ges.*, 21, 479, 615, 623 (1919); *Z. Physik*, 2, 1; 3, 437 (1920); 5, 410 (1921).

CHAPTER VI

FREQUENCY OF RADIATION, TEMPERATURE AND THE RATE OF PHOTOCHEMICAL REACTIONS

Among an extraordinary variety of phenomena disclosed by the studies of photochemical reactions, the influence of the wave length of absorbed radiation on the rate and course of photochemical reactions is of particular interest from a more physical point of view. Unfortunately, the investigation of this particular problem encounters considerable experimental difficulties and, therefore, only few exactly determined data are available on the subject. It is probably superfluous to point out once more the complete insufficiency in this particular respect of the so-called estimates, since, on previous pages, we have already met quite a number of reactions, which, on closer investigation, revealed entirely different relations than was assumed originally on the basis of "estimates" and qualitative experiments. Consequently, the following discussion will be restricted mainly to quantitative data obtained by simultaneous measurements of the rate of reactions and of the amount of absorbed monochromatic radiation.

According to the Einstein-Stark equivalence law the rate of a photochemical reaction in light of different wave lengths must vary as the number of absorbed light energy quanta. Experimentally, this prediction of the law has only been confirmed with a small number of photochemical reactions. Exact data over a wide spectral region are available on the decompositions of hydrogen iodide and bromide and on the reaction of iodine with ferrous ions. Photographic emulsions, the reaction of chlorine with carbon trichlorobromide, and the isomeric transformation of o-nitrobenzaldehyde into o-nitrosobenzoic acid have been investigated only over a narrow spectral region. All these reactions possess other simple kinetic relations, approaching closely the requirements of the equivalence law, as, for instance, the independence of the rate from the concentration of the reactant, more or less complete absence of catalytic influences, small temperature coefficients, and a quantum yield not far from unity. Conversely, we may now conclude that other reactions having the same simple characteristics, namely the decomposition of nitrosyl chloride, the decom-

positions of chlorine dioxide and monoxide in carbon tetrachloride solution, the decompositions of chlorine monoxide and of ozone sensitised by chlorine, the reaction of oxygen and carbon trichlorobromide sensitised by bromine, the decomposition of oxalic acid sensitised by uranyl salts, etc., will show, when investigated quantitatively, the same proportionality between the reaction rate and the number of absorbed quanta in different spectral regions. This prediction can be made with a considerable degree of probability since, according to the modern theories of quantised light absorption, and independent of the particular assumptions involved in the derivation of the equivalence law, the rate of all photochemical reactions in which the primary action of light is followed only by a few rapid and quantitative secondary processes, as in those reactions which have been now enumerated, the rate must be proportional to the number of light quanta absorbed. The survey of the remaining experimental material presented on earlier pages shows further that, apart from the particular group of reactions mentioned, very few possess the same characteristic relation between their rate and the wave length of absorbed radiation. The decomposition of aqueous chlorine solutions and, possibly, the oxidation of hydriodic acid [1] may be mentioned in this connection.

It would seem that the remaining photochemical reactions could be conveniently divided into two groups: those in which an increase of the wave length of absorbed radiation causes an increase and those where it causes a decrease of the quantum yield. Actually, however, reactions which proceed faster when smaller quanta are absorbed, are at least very scarce, if observed at all. More recent and exact measurements have disproved already, in a number of cases, the existence of a particular spectral sensitivity maximum, which, at one time,[2] was believed to be situated on the long wave side of "photochemical" absorption bands. It is very likely that the observed maximal sensitivity to a particular spectral region of a few other reactions not recently reinvestigated, as, for instance, the oxidation of quinine by chromic acid or the oxidation of iodoform by oxygen, is also entirely due to the joint action of the spectral distribution of the absorption bands of the reactant and of the radiation intensity of the light source used. The only sufficiently investigated reaction for which a similar explanation is inadequate is the oxidation of a series of organic acids by ferric salts. Winther, who studied this

[1] Comp., however, Winther, *Trans. Farad. Soc.*, 21, 459 (1925).
[2] Comp. Plotnikoff, *Z. physik. Chem.*, 79, 641 (1912); and Luther and Forbes, *J. Am. Chem. Soc.*, 31, 770 (1909).

reaction, made it probable, however, that the solutions of ferric chloride and organic acids investigated contain, besides a photochemically active component, another constituent which, absorbing light, acts as an inner filter. A similar factor affects also the quantum yield of carbon dioxide assimilation by green plants, a reaction which may be briefly mentioned here in this connection. Warburg and Negelein,[3] measuring the quantum yield, found, approximately equal values (0.230) for the wave lengths 6600 and 5780 Å. but a considerably lower yield (0.195) in light of the wave length 4360 Å. This anomalous decrease was attributed by the authors to a partial absorption of active radiation of the blue spectral region by yellow dyes present in the green leaves and participating in the assimilation process, if at all, to a lesser extent than the green dye chlorophyll. Quite recent experiments of Gaffron[4] support this suggestion of Warburg and Negelein, since they show that some oxidations, photosensitised by pure chlorophyll to visible light, have, indeed, a constant quantum yield independent of the wave length of absorbed radiation. Thus, probably in both reactions considered, the higher photochemical efficiency of longer waves is due entirely to the action of a factor which, in reality, is quite different from the photochemical sensitivity of a definite reaction. In the case of the isomeric changes of fumaric and maleic acids, finally, the variations of the quantum yield with wave length are rather small. At any rate, Warburg's experiments do not reveal a pronounced higher sensitivity of either of these reactions to light of longer waves.

Concluding, we may say that a higher photochemical efficiency of smaller light energy quanta is at least a very rare phenomenon.

In contrast to the very doubtful existence of this latter influence of the wave length on the rate of photochemical reactions, a higher effectiveness of larger light energy quanta has been frequently observed. Such reactions as the non-photosensitised decomposition of ozone, the decomposition of oxalate and other complex cobaltic salts, the maleic-fumaric ester transformation in the presence of bromine, the decomposition of hydrogen peroxide and bleaching of dyes and many others, have undoubtedly a higher quantum yield in light of shorter wave length. All these reactions show not only a very definite deviation from the strict requirements of the equivalence law, but are also in apparent disagreement with those broader conclusions concerning the rate of photochemical processes, which can be drawn from the

[3] *Z. physik. Chem.*, 106, 191 (1923).
[4] *Ber.*, 60, 775 (1927).

theory of quantised light absorption when combined with the experimentally demonstrated existence of secondary photochemical processes, not themselves light sensitive. In the following pages, some other of the representative photochemical reactions having variable quantum yields will be considered. The discussion should bring us nearer to a complete understanding of the phenomena underlying the observed decrease of quantum yield with decreasing energy of absorbed quanta.

Ozone Formation. Formation of ozone from oxygen under the action of light was originally studied by Lenard,[4a] who found that, at ordinary gas pressures, only the extreme ultraviolet radiation—below 2000 Å.—causes this reaction. Experiments of Regener [5] demonstrated that, under the influence of the total radiation of a spark discharge, a stationary state is gradually reached with a few per cent of the total oxygen present as ozone. Regener found, further, in agreement with earlier observations of Lenard, that only the extreme ultraviolet radiation was responsible for the formation of ozone and that this latter was decomposed mainly by the action of longer waves. Several quantitative investigations on the rate of ozone formation in monochromatic ultraviolet light were carried out by Warburg.[6]. In contrast to earlier investigators, he found that ozone can be formed by the action of radiation of a much longer wave length than 1900 Å., provided oxygen under high pressure is used and thereby a sufficient light absorption secured. In the following table, Warburg's determinations of the quantum yield at different oxygen pressures, using light of two different approximately monochromatic wave lengths, are presented.

TABLE 33.

	95 per cent O_2; 5 per cent N_2				Air: 21 per cent O_2; 79 per cent N_2	
Pressure Kg/cm² / Wave length	47.5	99–100	100–140	300	136–146	293
2070 Å.	1.03	0.92	0.91	0.77	0.93	0.65
2530 Å.	—	ca. 0.63	0.55	0.29		

[4a] *Ann. Physik*, 1, 486 (1900); see also Wilson; *Proc. Roy. Soc.*, 64, 127 (1898).
[5] *Ibid.*, 20, 1033 (1906).
[6] *Sitzb. Akad. Wiss.*, 216 (1912); 872 (1914); *Z. Elektrochem.*, 27, 133 (1921).

A quantum yield of unity would indicate the formation of two ozone molecules on absorption of one quantum of light energy, according to the equation:

$$O_2 + h\nu + 2O_2 \rightarrow 2O_3.$$

The table shows, however, that only in the light of mean wave length 2070 Å. and under pressures not exceeding 100 atmospheres is the quantum yield very close to unity. With increasing pressure, the yield drops steadily. More pronounced still is the drop of the quantum yield in the wave length region 2530 Å.. Here, even at lower pressures, considerably less than two molecules of ozone are formed per quantum of light energy absorbed. In the opinion of Warburg, who assumed the primary process, on light absorption, to be a dissociation of the oxygen molecule into atoms, the deviations of the quantum yield from unity are due mainly to two causes. The smaller yield, in light of the average wave length 2530 Å., is due to the energy quanta being smaller than the heat of dissociation of oxygen molecules.[7] On this view, activated molecules and not atoms are produced by this wave length and therefore (comp. 1st chapter, page 20) the yield is less than unity. The decrease of the quantum yield at higher oxygen pressures is caused, according to Warburg, by the influence exerted on the light absorbing molecules by the neighbouring ones. These are supposed to take up a part of the absorbed light energy and thus decrease the amount available for the chemical process. Warburg pointed out that the existence of such an influence on the part of neighbouring molecules is indicated, apart from the photochemical experiments, by deviations from Beer's law observed by him in oxygen at higher pressures. Actually, the absorption coefficient for the wave length 2070 Å. increases by 6.8-fold when the pressure is raised from 27.5 to 322.5 Kg/cm^2. A similar, although less pronounced, increase was observed for the wave length 2530 Å.

An investigation of ozone formation at low pressures of oxygen and on illumination by extreme ultraviolet radiation (1862-1719 Å.) was recently carried out by Eucken.[8] His experiments extended over a wide concentration interval and were mainly concerned with the influence of temperature on the rate of this reaction. The results are rather unexpected. Whereas the ozone yield at oxygen pressures close to atmospheric is practically independent of temperature, Eucken finds that, at concentrations below approximately 5×10^{-3} mols per liter, there is a much more rapid ozone formation at the temperature

[7] Warburg based his calculations on a value of 140,000 cal.
[8] *Z. physik. Chem.*, 107, 436 (1923).

of liquid air than at room temperature. Such a negative temperature coefficient of ozone formation, limited to low oxygen concentrations only, is explained by Eucken by assuming that the mean life of activated molecules, which are supposed to be formed on light absorption, depends on the temperature of the gas. These activated molecules then either undergo a reaction on collision—Eucken considers as most probable the two possibilities:

$$O_2' + O_2 \rightarrow O_4 \rightarrow O_3 + O$$
$$O_2' + 2O_2 \rightarrow O_6 \rightarrow 2O_3$$

—or they lose the activation energy by re-emission of absorbed radiation. It is unnecessary to discuss in detail the kinetic interpretation of such reaction mechanism, since, already on earlier pages, it has been shown that the resulting equation requires at lower concentrations, *ceteris paribus*, a proportionality of the reaction rate to the mean life of the activated molecules, whereas, at higher concentrations of the reactants, the rate is not influenced any more by this quantity. The conclusions which can be drawn from Eucken's assumption are thus in agreement with his own observations. The assumption is further not in disagreement with the results of spectroscopic studies, since the absorption of light by molecules causes a change not only of their electronic, but also of their rotational energy. These changes are, however, small [9] and the rotational energy of activated molecules is not very different from that of normal ones. It is thus a function of the temperature of the light absorbing gas, so that the mean life of activated molecules will also be a function of the temperature if it is influenced by the rotational energy. Eucken finds actually, in known band spectra, some indications, that the larger the rotational energy of activated molecules, the shorter their mean life is.

A recent study of the absorption spectrum of oxygen by Birge and Sponer [10] seems to support Eucken's assumption that activated molecules, and not oxygen atoms, are formed on absorption of those wave lengths of which the photochemical action has been studied so far. According to Birge and Sponer only light below about 1751 Å. causes a dissociation of oxygen molecules. The products of this process, as in the case of halogens, are probably a normal and an excited oxygen atom. It cannot be denied that, besides such dissociation in one elementary act, another process is conceivable, namely,

[9] Normally the rotational quantum number changes by ± 1. Lenz; *Physik. Z.*, **21**, 691 (1920).

[10] *Phys. Rev.*, **28**, 259 (1926).

a dissociation into two normal atoms induced by molecular collisions of activated oxygen molecules, a process which requires smaller light energy quanta. The heat of dissociation of oxygen molecules into normal atoms is, however, not much less than 162,000 cal. according to Birge and Sponer and therefore, even if such a process is possible in general, it certainly cannot be caused by light of those wave lengths which were employed by Warburg for his experiments (the energy quanta of wave length 2070 Å. have about 140,000 cal. per mol, those of the wave length 2530 Å. about 112,000 cal.).

Thus, it must be concluded that the difference in the quantum yields for these two wave lengths cannot be attributed to different processes occurring on absorption of light energy, since on absorption of either wave length the same activated molecules are produced. The difference in quantum yield can be due, therefore, only to the difference in the energy content of these activated molecules. It must be admitted, however, that the details of the resulting reaction mechanism are still unknown. It is rather improbable that ozone is formed by a trimolecular collision according to the equation:

$$O_2' + 2O_2 \rightarrow 2O_3,$$

since then, instead of a decrease, an increase of the quantum yield with pressure would be anticipated. On the other hand, if the reaction is:

$$O_2' + O_2 \rightarrow O_3 + O \quad (O + O_2 \rightarrow O_3),$$

the falling yield in the neighbourhood of the wave length 2530 Å. can be attributed to the activation energy being slightly smaller than or equal to the heat of this process,[11] so that only a fraction of all the collisions of activated molecules is successful, the rest being followed by degradation of energy.

The Decomposition of Nitrates in Solution. The decrease of the quantum yield for longer light waves is particularly pronounced in several photochemical reactions occurring in aqueous solutions. The decomposition of nitrates in ultraviolet light has been studied by many investigators. The result of earlier researches [12] was the observation that nitrites and molecular oxygen are formed and that the reaction is represented by the stoichiometric equation

$$2NO_3^- \rightarrow 2NO_2^- + O_2.$$

A quantitative study of this reaction has been carried out by War-

[11] About 118,000 cal., if $O_2 \rightarrow 2O$ requires 162,000 cal.

[12] Thiele, *Ber.*, **40**, 4914 (1907); Lombard, *Compt. rend.*, **150**, 228 (1910); Berthelot and Gaudechon, *ibid.*, **152**, 522 (1911); Baudisch, *Ber.*, **44**, 1009 (1911).

burg.[13] His experiments with polychromatic light showed that the rate of decomposition is much faster in alkaline than in acid solutions of nitrates. Warburg's measurements of the quantum yield extended over three wave lengths and different concentrations of potassium nitrate in 0.0033 *N* sodium hydroxide solution and revealed that, under all circumstances, less than one molecule of nitrate is decomposed per absorbed light quantum. The actual data are given in Table 34.

TABLE 34.

0.0033*N* NaOH.

Concentration \ Wave length	2070	2530	2820 Å.
0.33*N* KNO_3	0.25	0.17	0.024
0.033*N*	0.19		
0.0033*N*	0.10		

These results of Warburg were later called into question by Anderson,[14] who suggested that the decomposition of nitrates is not complete and that a photochemical stationary state is reached on prolonged illumination.

The question was solved recently by Villars,[15] who succeeded in showing the correctness of Warburg's experiments and, furthermore, extended considerably the measurements of quantum yield. Improving Warburg's experimental conditions, Villars studied the rate of decomposition of nitrates in solutions of definite hydrogen ion concentration. Results obtained on the influence of pH on the quantum yield, measured in light of the wave length 2540 Å., are given in Figure 7. The influence of the wave length was also investigated by Villars over a wide spectral region. His data, which are in good agreement with those of Warburg, are represented in Table 35.

TABLE 35.

KNO_3 1.0*N* pH = 9.9

Wave length Å.	2540	2700	2800	3020	3130	3350	3660
Quantum yield	0.30	0.07	0.024	0.013	0.010	0.014	0.00

The quantum yield falls off extraordinarily rapidly at wave lengths above 2500 Å. The relatively high quantum yield obtained with the line 3350 Å. is due in all probability, as Villars pointed out, to the

[13] *Sitzb. Akad. Wiss.*, 1228 (1918).
[14] *J. Am. Chem. Soc.*, 46, 797 (1924); comp. also Suryanarayana, *J. Sci. Assoc. Maharajah's College*, Vizianagaram 2, 12 (1924).
[15] *J. Am. Chem. Soc.*, 49, 326 (1927).

action of some scattered light of shorter wave length and would be much smaller if a pure monochromatic radiation of this wave length were isolated.

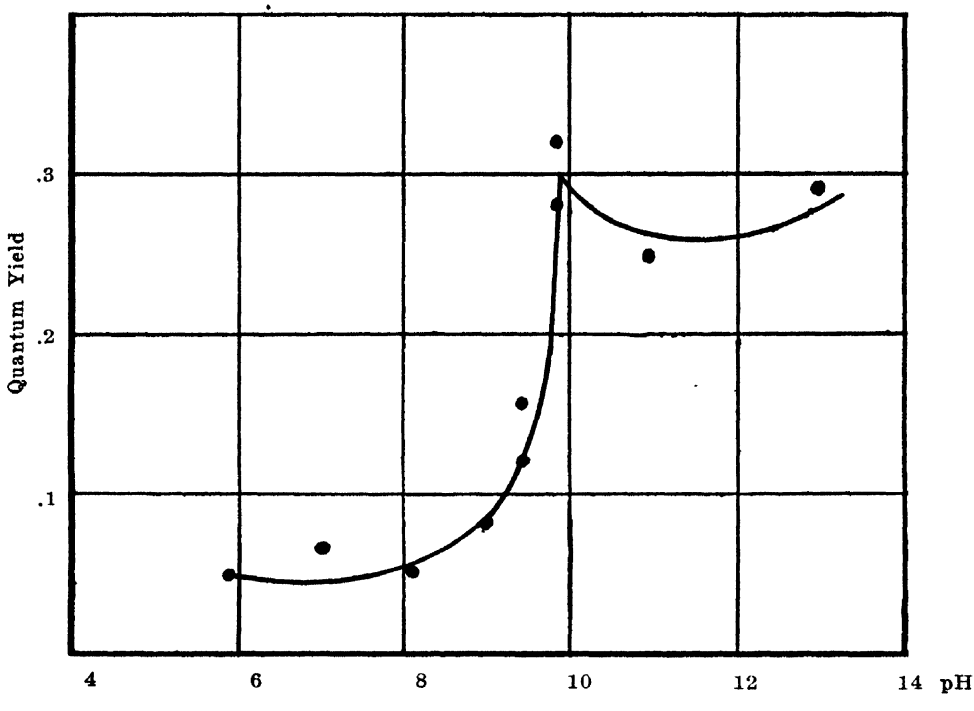


FIGURE 7.—The Relation of the Quantum Yield to pH in 1 *M* KNO_3; Light 2536Å.

In the opinion of Warburg, the chemical process which follows the absorption of light energy quanta by nitrate ions is a unimolecular dissociation according to the scheme:

$$NO_3^- + h\nu \rightarrow (NO_3^-)' \rightarrow NO_2^- + O.$$

This process requires, as Warburg calculated, about 100,000-90,000 cal., and, thus, at least quanta of wave length 2800-3150 Å.[16] To account for the quantum yield being much smaller than unity, Warburg suggested that the activated nitrate ions may lose their energy before reacting by inelastic collisions. This process must happen particularly frequently when the absorbed light energy is only slightly larger than or equal to the heat of decomposition, since, under such circumstances, even a relatively small loss of energy will prevent the chemical process. Thus, a rapid decrease of the quantum yield in the spectral region beyond 2800-3150 Å. should be anticipated and has been actually observed by him. Despite this apparently very good agreement

[16] The more probable value for the heat of dissociation of oxygen 162,000 cal. changes the wave length limit to 2500-2700 Å.

with experiment, Warburg's theory is not entirely satisfactory. In particular, the agreement will be entirely lost if the recent value for the heat of dissociation of oxygen (*cf.* above) be accepted. Comparing Villar's data, and even neglecting the value for wave length 3350 Å., we still find that the reaction proceeds with measurable velocity even when the absorbed activation energy has a deficit of some 12,000-22,000 cal. as compared with the heat required by the unimolecular process.

The influence of the hydrogen ion concentration on the quantum yield, as revealed particularly in Villars' experiments, can hardly be accounted for by Warburg's suggestion that the undissociated nitric acid molecules are, under otherwise identical conditions, less easily decomposed photochemically than the nitrate ions. Further, the decrease of the quantum yield with nitrate concentration, observed by Warburg, cannot be attributed to variations in the hydrogen ion concentration.[17] It indicates rather the existence of some other process besides the assumed unimolecular dissociation of the nitrate ion.

Hydrolysis of Chloroplatinic Acids. The sensitivity of different chloroplatinic acids to light was noticed by Kohlrausch,[18] according to whom the reaction is a hydrolysis leading to formation of platinic hydroxide and hydrochloric acid. The photochemical reaction of chloroplatinic acids was later thoroughly investigated by Boll and Job,[19] by Boll [20] and by Boll and Henri.[21] Their results indicate that light causes, not a direct formation of platinic hydroxide, as was suggested by Kohlrausch, but at least an intermediary formation of a complex containing two atoms of platinum, the reaction being represented by the generalised stoichiometric equation:

$$2(PtCl_n(OH)_{6-n})H_2 + (2n-1)\,H_2O \rightarrow (2n-1)HCl + [PtCl(OH)_5H_2;\ Pt(OH)_6H_2]$$

The study of the kinetics of the process revealed further, that in dilute aqueous solutions ($2 \times 10^{-5} - 2 \times 10^{-4}$ normal with respect to the acids), in which the light absorption was incomplete, the rate of hydrolysis was bimolecular and proportional to the incident light intensity. These observations indicate of course that the quantum yield, being independent of light intensity, is proportional to the concentration of the acids. Although light causes, in the solutions of all acids studied, the formation of the same final product, the rate of

[17] Comp., however, Villars, *loc. cit.*
[18] *Z. physik. Chem.*, 33, 257 (1900).
[19] *Compt. rend.*, 154, 881 (1912); 155, 826 (1912).
[20] *Ibid.*, 156, 138 (1913; 156, 691 (1913); 157, 115 (1913).
[21] *Ibid.*, 158, 32 (1914).

this reaction decreases for different chloroplatinic acids under identical conditions of illumination and concentration in the order:

$$[PtCl_5(OH)]\,H_2;\ [PtCl_6]\,H_2;\ [PtCl_4(OH)_2]\,H_2;\ [PtCl_2(OH)_4]\,H_2.$$

Very thorough measurements of Boll revealed that an extraordinarily wide spectral region is active in all these hydrolytic reactions, but that the efficiency of radiation per unit of energy absorbed rapidly decreases with increasing wave length. The following table represents Boll's results and, in addition, newly calculated quantum yields of the hydrolysis of tetrachlorplatinic acid, on which reaction the most complete data are available.

TABLE 36. $[PtCl_4(OH)_2]\,H_2$ 0.0001*N*.

Wave length Å.	2378	2400	2482	2537	2655	2970	3100	3660	4350	5460
$\frac{\text{Rate}}{\text{Energy absorbed}}$	(4.4)	(3.5)	2.8	1.9	1.6	0.29	0.086	0.038	0.0057	0.0020
Quantum yield .	(4.7)	(3.7)	2.8	1.9	1.5	0.25	0.070	0.026	0.0033	0.0009

Very similar results were obtained by Boll for the hexachlor- and dichlor-platinic acids.

Little is definitely known concerning the mechanism of these reactions. The proportionality of the quantum yield to the concentration of the acids and the composition of the reaction product could be interpreted as indicating that the chemical process is a bimolecular reaction, which takes place on the collision of molecules activated by absorption of light energy with other acid molecules. However, the quantum yield apparently can exceed two under favourable conditions (high concentrations of the reactants and light of short wave lengths) and the reactions must therefore have a chain mechanism. The fraction of molecules activated by absorption of light energy which enter into reaction may be considerably smaller than indicated by the values in Table 36, if an activated molecule starts a relatively long chain of other reacting acid molecules each time. In such a case it is conceivable that the primary reaction involves, besides water, only one (the activated) platinic acid molecule and that the variable length of subsequent chains determines the proportionality of the "apparent" quantum yield to the concentration of the acid.

On the other hand, the relation of the yield to the frequency of absorbed radiation can hardly be explained by a varying length of the hypothetical chains. Once these secondary reactions have been somehow started by the primarily activated acid molecules, they will

require for their completion no further action of light.[22] The length of the chains will be completely determined by the concentrations of all reactants and the temperature in accordance with the laws of chemical kinetics and will be hardly affected in any way by the size of the primarily absorbed quanta. Consequently, since the length of the chains remains essentially constant, it must be their number relative to the number of absorbed quanta that varies with the energy content of the latter. In other words, it must be concluded that the probability of a primarily activated molecule being deactivated before reaction increases very rapidly with decreasing size of absorbed quanta.

The hydrolysis of the chloroplatinic acids, being sensitive to an unusually wide range of wave lengths, is unquestionably a very convenient object for a detailed study of the mechanism of deactivation and its relation to the energy content of activated molecules.

The Decomposition of Oxalic Acid. A comparison of reactions in aqueous solutions of oxalic acid already discussed shows that the kinetics of the photochemical processes depend largely on the nature of the other reactants present. Thus, in the presence of uranyl salts, the reaction satisfies very closely the requirements of the equivalence law, whereas mercuric and ferric salts induce chain reactions of complicated and not fully established character. In contrast to these reactions, the decomposition of pure oxalic acid solutions is very slow. Berthelot and Gaudechon,[23] who were the first to investigate this decomposition in detail, found that the course of the reaction is dependent on the spectral distribution of the incident radiation. Thus, in light of longer wave length than 2500 Å. formic acid and a gaseous mixture containing about 89 per cent carbon dioxide and 11 per cent carbon monoxide were formed, whereas in light of shorter wave lengths the products of reaction were CO_2 67 per cent, H_2 33 per cent and traces of formaldehyde.[24] Berthelot and Gaudechon interpreted their results by suggesting that oxalic acid is quantitatively decomposed according to the equation:

$$H_2C_2O_4 \rightarrow HCOOH + CO_2$$

by rays below about 3000 Å. and that the formic acid produced undergoes also a photochemical decomposition, either by:

$$HCOOH \rightarrow H_2O + CO$$

[22] This, of course, is only an assumption, but one which is supported by the studies of other photochemical reactions.
[23] *Compt. rend.*, 158, 1701 (1914).
[24] Observed also by Baly, Heilbron and Barker, *J. Chem. Soc.*, 119, 1025 (1921).

in light of the wave length region 2500-3000 Å. or by

$$HCOOH \rightarrow H_2 + CO_2$$

in extreme ultraviolet. Recently Allmand and Reeve [25] repeated and extended these earlier experiments of Berthelot and Gaudechon, studying, however, only the initial stages of the reaction, working thus under conditions excluding a secondary decomposition of the reaction products. In agreement with the earlier conclusions of Berthelot and Gaudechon, Allmand and Reeve found that oxalic acid is quantitatively decomposed into formic acid and carbon dioxide. Neither carbon monoxide nor hydrogen could be detected among the gaseous products of the reaction, but, instead, small amounts of formaldehyde were found. The amount of this latter relative to carbon dioxide was further found to increase very considerably in light of shorter wave lengths. Studying the effectiveness of different wave lengths in the oxalic acid decomposition, Allmand and Reeve found, in contrast to observations made by Berthelot and Gaudechon, that light of longer wave length than 3000 Å. is also active photochemically. The quantum yield, however, decreases very considerably with increasing wave length. In the following table are given the calculated values, which must be considered as approximations, since, in all determinations, a relatively wide spectral region was used for illumination.

TABLE 37.

Wave length	2650	3000	3650 Å.
Quantum yield	0.0100	0.0041	0.00095

The above values were determined for solutions 0.6-0.7 normal. A few experiments, made with more dilute solutions, indicate, although not very definitely, that, in these, the yield is higher. Discussing possible causes of formaldehyde formation, Allmand and Reeve suggested that the carbon dioxide molecules formed on decomposition of oxalic acid may contain initially a large excess of energy and may react occasionally with water according to the equation:

$$CO_2 + H_2O \rightarrow HCOH + O_2.$$

On the basis of this suggestion, they attributed the accelerating action of short rays on formaldehyde formation to higher energy content, and thus to the increased reactivity of the newly formed carbon dioxide molecules. The contrast is striking between the quantum yields for pure oxalic acid solutions, as determined by Allman and Reeve, and the yield of unity obtained by Büchi for oxalic acid

[25] *J. Chem. Soc.*, 129, 2834 (1926).

solutions in presence of uranyl salts, since, in both cases, the main reaction is a chemically identical process of oxalic acid decomposition, the reduction of uranyl ions in Büchi's experiments playing only an unimportant rôle. No definite explanation of this variable behaviour is possible at present and we may only say that, in the uranyl-oxalic acid complex, the latter must be better protected against loss of activation energy on inelastic collisions than when present in solutions as free molecules, and that this is possibly connected with the fact that, in the complex, not the oxalic acid but the uranyl ion is primarily responsible for the absorption of visible and near ultraviolet light which alone has been studied in this case.

It may be mentioned here, that the decomposition of solid oxalic acid, studied already by Berthelot and Gaudechon,[26] shows, according to Noyes and Kouperman,[27] the same increasing rate in light of shorter wave length as is shown by the aqueous solutions of the acid. In the reaction of solid oxalic acid, water apparently plays the rôle of a catalyst. Anhydrous acid was found to decompose more slowly than the hydrated crystals.

Decomposition of Formic Acid. In the preceding section, the suggestion of Berthelot and Gaudechon was noted that the carbon monoxide and hydrogen observed by them during oxalic acid decomposition were, in reality, the products of reaction of formic acid and that this latter could be decomposed in two different ways depending on the frequency of the absorbed radiation. Recently, Allmand and Reeve [28] have investigated, in connection with their studies on oxalic acid decomposition, the processes taking place by the action of light on aqueous solutions of formic acid and have arrived at results which are in definite disagreement with the proposed theory of Berthelot and Gaudechon. An analysis of the reaction products, carried out by Allmand and Reeve, showed that these, or at least their relative amounts, depend largely on the concentration of the formic acid solution, but not on the wave length of absorbed radiation. Thus, a 2.4 *N* solution yielded preponderantly carbon dioxide, much formaldehyde, its condensation and reduction products and only small amounts of carbon monoxide and of hydrogen. On the other hand, in a 0.113 *N* solution the yield of carbon monoxide and hydrogen relative to carbon dioxide was markedly increased but no formaldehyde was formed. Discussing these results, Allmand and Reeve suggested that formic acid molecules can be decomposed in two different ways inde-

[26] *Compt. rend.*, **152**, 262 (1911); **158**, 1791 (1914).
[27] *J. Am. Chem. Soc.*, **45**, 1398 (1923).
[28] *J. Chem. Soc.*, **129**, 2852 (1926).

pendent of the wave length of absorbed radiation. The alternative reactions are:

$$HCOOH \rightarrow CO_2 + H_2$$
$$HCOOH \rightarrow CO + H_2O.$$

A comparison of the relative amounts of the different gases formed on decomposition of dilute formic acid solution indicates that the first reaction occurs about 6 times more frequently than the second one. The deficiency of carbon monoxide and hydrogen and the presence of formaldehyde among the decomposition products of the more concentrated formic acid solution indicates that secondary reactions are taking place. Allmand and Reeve are of the opinion that among the molecules formed in the primary decompositions of formic acid, hydrogen and carbon monoxide possess initially large amounts of energy and are capable of reacting on collision with acid molecules:

$$(1)\quad H_2' + HCOOH \rightarrow HCOH + H_2O$$
$$(2)\quad CO' + HCOOH \rightarrow CO_2 + HCOH.$$

In more dilute solution, on the other hand, these activated molecules lose their energy by collision with water before meeting formic acid molecules; therefore, no secondary reactions take place. The multiplicity of processes involved in formic acid decomposition is apparently not exhausted by those already discussed, since the quantum yield measurements indicate that, in light of wave length 2600 Å. (mean) and independent of concentration, more than two formic acid molecules are decomposed on absorption of one energy quantum. Allmand and Reeve conclude that the primary decomposition products which contain, as the result of absorption of large quanta by the formic acid molecules, a large excess of energy, are capable not only of reacting in the manner suggested above, but also of transmitting their energy to other formic acid molecules on collision, thus causing short reaction chains. It is not very well understood how this particular reaction can be independent of the acid concentration as it must be, the quantum yield being found constant, since the authors themselves were forced to postulate that the activated molecules lose their energy on collisions with water in more dilute acid solutions. Quantum yields, calculated by Allmand and Reeve, as in the case of oxalic acid decomposition for an average wave length of a relatively wide spectral region, are represented in Table 38.

TABLE 38. Formic Acid 2.4 *N*.

Wave length	2600	3000	3600 Å.
Quantum yield	2.7	1.06	very small

These values, as compared with those of oxalic acid decomposition, show a rather interesting peculiarity, namely, that the quantum yield of formic acid decomposition decreases extraordinarily rapidly in the spectral region 3000-3600 Å., whereas the ratios of the yields of both acids for the wave lengths 2600 and 3000 Å. are practically the same.

Decomposition of gaseous formic acid has been investigated by Ramsperger and Porter.[29] They find that in total radiation of a mercury arc transmitted by quartz, 64 per cent of $CO + H_2O$ and 36 per cent of $CO_2 + H_2$ are present after the acid has been completely decomposed. Their observation becomes particularly interesting when compared with the data of Allmand and Reeve, because it shows that the relative rates of the two types of decomposition:

$$(1)\quad HCOOH \rightarrow CO + H_2O$$
$$(2)\quad HCOOH \rightarrow CO_2 + H_2$$

are quite different in the gaseous state and in the aqueous solution. It should be mentioned here that Taylor and Bates,[30] investigating the decomposition of the formic acid vapour sensitised by mercury atoms, thus in monochromatic light 2536 Å., found again a different ratio $(CO + H_2O) : (CO_2 + H_2) = 76:24$. A future investigation of the true causes of these varying relative rates of decomposition of the same molecule will solve one of the most important general problems of photochemistry.

General Considerations. In the preceding pages, we have set forth different theories treating in a more or less general way the observed decrease of the quantum yields with frequency of absorbed radiation. Warburg, for instance, attributes it to the energy content of quanta approaching and falling below the minimum energy required for a unimolecular dissociation process in the light absorbing molecules. The theory, however, even if applicable to a limited number of photochemical reactions, fails entirely in all those cases where the quantum yield decreases steadily over a wide spectral region, as for instance in the hydrolysis of chloroplatinic acids. In their general theory of chain reactions [31] Christiansen and Kramers suggested that the energy of absorbed quanta, increased by the heat of reaction, is stored up in the newly formed molecules and may be transmitted by them through collisions to other reactant molecules. It has already been pointed out that Allmand and Reeve, accepting this general point of view, emphasised the point that, with increase in the energy content of the

[29] *J. Am. Chem. Soc.*, 48, 1267 (1926).
[30] *Loc. cit.*, comp. page 132.
[31] Comp. first chapter, p. 21.

absorbed quanta, the energy of the reaction products and therefore their reactivity must also increase. They interpreted the quantum yield greater than two in the case of formic acid in this manner. It is difficult to reconcile with this theory the observation of Allmand and Reeve that the quantum yield remains the same when the concentration of formic acid is being decreased. On account of the deactivating action of collisions with water molecules a decrease of the yield with concentration would be expected. Lasareff,[32] Henri,[33] and others have assumed repeatedly that the rate of photochemical reactions is proportional, not to the number of absorbed quanta, but to the amount of light energy absorbed. Such a relation, of course, means a decrease of the yield with frequency of radiation, but the resulting changes are rather small.

Boll,[34] in connection with his studies of the hydrolysis of platinic acids, suggested a logarithmic relation between the rate of reaction and frequency of radiation: $\log k = -a\nu + b$, without giving a kinetic interpretation of such relation.

For a better comparison of the experimental material available on the subject under discussion, the data are summarised graphically in Figure 8, in which the logarithms of quantum yields are plotted against frequency of radiation (or the energy content of the quanta). Figure 8 shows evidently that neither the proportionality of the rate to the absorbed light energy, nor the logarithmic function of Boll, represents the actual conditions. They seem to be more or less specific for each reaction. Such behaviour would be expected since several factors contribute undoubtedly to the phenomenon. Their analysis, apart from the suggestions already mentioned, has not been carried out. We might be tempted to attribute the decrease of quantum yield in a general way to a more ready loss of activation energy or to a diminishing probability of reaction on absorption of smaller energy quanta, but such suggestions remain somewhat formal unless a more detailed kinetic interpretation of the phenomena can be given. Another possibility which cannot be denied *a priori* is contained in the suggestion that, within a spectral absorption region, molecules in different initial quantum states (vibrational and rotational) can absorb radiation, but only molecules which were in a definite quantum state can be activated by absorption of light energy to chemical reaction. The variations of the quantum yield are thus reduced to an "inner light filter" action on the part of non-active reactant mole-

[32] *Trans. Farad. Soc.*, **21**, 475 (1925).
[33] *Compt. rend.*, **156**, 1012 (1913).
[34] *Ibid.*, **157**, 115 (1913).

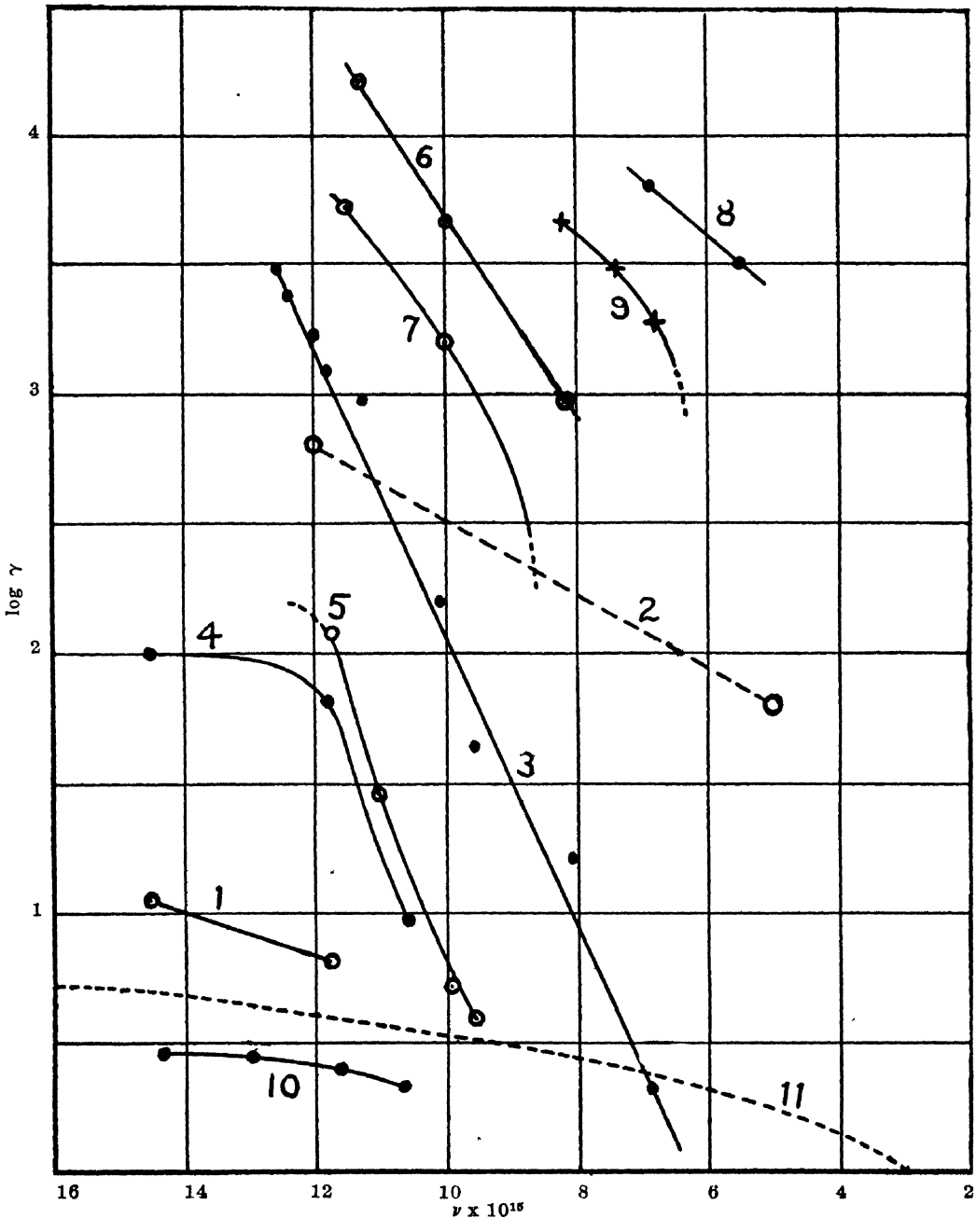


FIGURE 8.—The Relation of the Quantum Yield to the Frequency of Radiation. Log γ plotted against frequency of radiation ν. Quantum yields (γ) in arbitrary units.

1. Ozone formation.
2. Ozone decomposition.
3. Chloroplatinic acid hydrolysis.
4. Nitrates 0.33*N* (Warburg).
5. Nitrates 1.00*N* (Villars).
6. Oxalic acid.
7. Formic acid.
8. Maleic-fumaric ethyl esters and bromine.
9. Cobaltic salts.
10. Hydrogen peroxide decomposition.
11. Proportionality to the absorbed energy.

cules. It will become evident, however, from the subsequent discussion of Tolman's theory that this assumption can be valid only in those cases in which a measurable temperature coefficient of the reaction rate has been observed.

Photochemical Threshold Frequencies. Theoretical considerations, based on quantum theory, have led several investigators in the course of the last fifteen years to the conclusion that, for every photochemical reaction, a limiting frequency of radiation must exist below which the radiation ceases to be photochemically active. According to the equivalence law, in particular, a sharp photochemical threshold would be expected, the quantum yield changing almost instantaneously from a constant value to zero. Experimental evidence on the subject is, however, very scarce, due partly to light absorption becoming immeasurably small at wave lengths shorter than the expected threshold of many reactions. In other reactions, summarised in Figure 6, a decrease of the quantum yield over wide spectral regions has been observed in place of a threshold. In particular, the decomposition of oxalic and formic acids have been found by Allmand and Reeve to proceed at a measurable rate in light of wave lengths much longer than those computed by Volmar [35] from thermochemical data on the heats of unimolecular decomposition and found by him to be in good agreement with the earlier observations of Berthelot and Gaudechon. By analogy, it seems probable that the apparent thresholds found by these investigators [36] in a number of organic photochemical decompositions will be found, on closer investigation, to show a steady decrease of the reaction rate due to the combined action of decreasing quantum yield and diminishing light absorption of light of lower frequencies. A single reaction in which a definite threshold in a continuous absorption region seems to exist is the combination of dry chlorine and hydrogen already discussed (comp. page 87). With this possible exception, the existence of a photochemical threshold, in the strictly defined meaning of the term, has not been confirmed by experiment. Quite different relations will be found, however, if the photochemical action of wider spectral regions be considered, in which regions several absorption bands, or systems of bands, of the reactant are situated. Abundant experimental material, already indicated, as for instance the inactivity of the red region of the absorption spectrum of chlorine, of the visible absorption bands of permanganate ion, etc., furnish a sufficiently solid basis for the conclusion that, normally, only a part

[35] *Compt. rend.*, 178, 679 (1924); 180, 1172 (1925).
[36] *Ibid.*, 151, 1349 (1910); 154, 1597; 155, 207, 401 (1912).

of the absorption spectrum is photochemically active in a given reaction. Plotnikoff [37] went farther and drew a strict distinction between photochemical and thermal absorption bands of a molecular species. His conclusion, however, is not entirely correct as is shown, for instance, by the photochemical reduction of Fehling's solution. Byk,[38] who initially investigated this reaction, found that only frequencies belonging to an ultraviolet absorption band of the cupri-complex are photochemically active. More recently Leighton [39] demonstrated that if hydroquinone be added to Fehling's solution the reduction can be produced also by light of the visible absorption band of the blue complex. Obviously, the lower limit of photochemical activity of radiation—a photochemical threshold in the broad sense of the word—is not entirely determined by the composition of the light absorbing reactant, but depends also, even if to a lesser degree, on the character of the reaction. In most of the known photochemical reactions, the inactive absorption region is situated on the longer wave length side of the investigated range of radiation frequencies. An interesting exception is the decomposition of acetaldehyde, for which Henri and Wurmser [40] found that only light of the middle ultraviolet was active photochemically. The extreme ultraviolet was not active, although equally absorbed. According to these authors, two atomic groups in the acetaldehyde molecule, the carbonyl and the methyl, have separate absorption bands, but only light energy absorbed by the first of these groups, having its absorption band in the middle ultraviolet, can be converted into chemical energy. Light energy absorbed by the methyl group is transformed into heat.

The existence of different light absorbing centres in a single molecule suggests, further, the possibility of several distinct photochemical processes caused in the same light absorbing molecule by light of different frequencies. This problem is undoubtedly of considerable interest, but unfortunately very little experimental work has been done in this direction. Besides the investigation of Henri and Wurmser on formaldehyde reaction and some rather uncertain data of Berthelot and Gaudechon, the observations of Taylor and Bates (page 132) on the decompositions of a number of organic molecules in presence and absence of mercury vapour are of interest. Although Taylor and Bates find a marked difference between the relative yields of gaseous reaction products of the direct and photosensitised reactions

[37] "Lehrbuch der Photochemie."
[38] *Z. physik. Chem.*, 49, 659, 679 (1904).
[39] *J. Phys. Chem.*, 17, 205 (1913).
[40] *Compt. rend.*, 156, 230 (1913); see also page 120; compare, however; Berthelot and Gaudechon, *Compt. rend.*, 156, 68, 233 (1913).

in several of the cases investigated, it still remains doubtful whether such difference is actually due to the varying energy content of quanta absorbed either by the mercury atoms or by the organic molecules themselves or whether it is due to the change in the conditions of the energy transfer to these reacting molecules. In particular, as was earlier pointed out, the excitation energy of mercury atoms can be transferred to colliding molecules as kinetic energy, whereas energy directly absorbed as radiation must necessarily appear in the form of internal energy.

The Photo-Activity of Infra-Red Radiation. In the preceding, the discussion of the chemical actions of radiation was limited to a relatively narrow spectral region comprised between the "extreme ultraviolet" of a wave length near to 1800 Å. and the long wave side of the visible spectrum, this range of frequencies being experimentally particularly easily isolated for photochemical purposes. Attempts, however, to study the actions of infra-red rays on the one side and X-rays on the other side of this well investigated spectral region are not entirely lacking. Particularly in recent years, a considerable interest in the activity of infra-red rays was stimulated by the theoretical considerations of Trautz,[41] Lewis,[42] Perrin[43] and others who developed the so-called radiation theory of chemical reactions. A discussion or criticism of the details of the original theory or its more recent modifications[44] will not be attempted here. It is sufficient for our purpose to mention that, generally, the molecular activation energy necessary for a reaction and which is calculated from Arrhenius' expression for the temperature coefficients of thermal reactions:

$$\frac{d\ ln\ k}{dT} = \frac{Q}{RT^2};\ k = c.e^{-Q/RT}$$

was expressed in terms of quantum energy with the aid of Einstein's relation: $Q = Nh\nu$. It was further assumed that the activation of reacting molecules occurred on absorption of quanta of the frequency ν from the black body radiation in equilibrium with the reacting mixture. In such manner the calculated "chemically active" frequencies fall in the infra red spectral region for the majority of thermal reactions proceeding at a measurable rate at room temperature and not far above it. Actually, a good agreement between calculated and experimentally determined absorption bands of the reactants was obtained in several cases, but, on the other hand, it was generally

[41] *Z. anorg. Chem.*, **102**, 81 (1918) and earlier.
[42] *J. Chem. Soc.*, **113**, 471 (1919) and earlier.
[43] *Ann. Physik*, **11**, 1 (1919).
[44] Comp. Tolman, *J. Am. Chem. Soc.*, **47**, 1549 (1925).

observed that even a manyfold increase in density of these "active" frequencies over the corresponding density of the isothermal black body radiation, did not affect the rate of reactions.[45] The few exceptions to this conclusion, as, for example, the positive results obtained by Rideal and Hawkins [46] in the hydrolysis of esters are undoubtedly erroneous.

Results of modern studies of the origin of absorption spectra, which attribute the infra-red absorption bands of molecules usually to changes in vibrational and rotational energy only, when combined with the generally accepted non-existence of the photochemical action of infra-red rays, force us to the conclusion that, for chemical activation of molecules on light absorption, a change in electronic energy is also necessary.

Chemical Action of X-rays. Chemical actions of X-rays on organic and inorganic matter were noted soon after the discovery of the rays, but, owing to considerable experimental difficulties, only few reactions have been investigated in more detail. In particular the study of gaseous reactions is handicapped by the small absorption coefficients which gases possess in the range of X-ray frequencies usually obtained. The large energy of these quanta is sufficient not only for the excitation of gaseous molecules—an effect which may be considered as normal for the visible and ultraviolet radiation—but also for complete separation of electrons from the sphere of the forces of atomic attraction. Thus, as the result of X-ray absorption, gaseous ions are usually produced. The action of an absorbed X-ray quantum does not cease with the formation of a pair of ions.

The expelled electrons have a large amount of kinetic energy and cause secondary ionisation. Another process which contributes to the quantum yield of ionisation is the atomic scattering of X-rays. According to Compton, a definite fraction of scattered radiation energy is transformed by scattering into kinetic energy of electron movement and the rest becomes radiation of lower frequency and thus of smaller quantum energy. Such repeated processes will of course result in the end in the formation of several ions per scattered quantum. Much experimental attention has been concentrated on a detailed study of the conditions of ionisation of gases by X-rays, but, for the purpose of this book, the above preliminary remarks are sufficient.

The only reaction in gases under influence of X-rays which has been studied is the combination of chlorine and hydrogen. LeBlanc

[45] Daniels and Johnston, *J. Am. Chem. Soc.*, 43, 1288 (1921); H. A. Taylor, *ibid.*, 48, 577 (1926); Daniels, *ibid.*, 48, 607 (1926).
[46] *J. Chem. Soc.*, 117, 1288 (1920).

and Volmer [47] found that in a light sensitive mixture as many as 10^4 molecules of hydrogen chloride are formed per pair of ions produced by X-rays and that, therefore, this reaction must have a chain mechanism. Kinetics of the reaction have not been investigated by LeBlanc and Volmer, but it is more than probable that they are similar to those found by Taylor [48] and later by Porter, Bardwell, and Lind [49] in the reaction induced by α-particles from a radioactive source, since in both cases, primarily, the same gaseous ions are produced. Of interest is the striking analogy between these reactions and that caused by ordinary light. Thus, Taylor obtained for the rate of hydrogen chloride formation the expression:

$$\frac{d\,[2HCl]}{dt} = k\,\frac{\epsilon_{abs.}\,[Cl_2]}{[O_2]}$$

which is identical with the equation obtained by Bodenstein for the rate of photochemical reaction. The analogy between these two reactions was extended even further by the recent investigation of Porter, Bardwell and Lind. These authors established more definitely than ever the chain character of the photochemical reaction by showing that this and the radiochemical reaction both followed the same kinetic equation and moreover that, at room temperature, each ion produced by impact of an α-particle yielded under all circumstances of gas sensitivity twice as many hydrogen chloride molecules formed as an absorbed light energy quantum. Of interest further is their observation that the temperature coefficient of the radiochemical reaction is considerably smaller than that of the photochemical, with the result that, at 100°, the numbers of hydrogen chloride molecules formed per ion formed or light energy quantum absorbed are nearly equal.

The action of X-rays on organic matter has been frequently utilised for medical purposes and investigated from this point of view, but no kinetic studies of definite reactions have ever been carried out. A typical example of the action of X-rays on inorganic solid compounds is the sensitivity of photographic plates to these rays. Recently Eggert and Noddack [50] estimated that as many as 1000 silver atoms are produced per quantum of X-radiation absorbed. Their estimate shows, obviously, that the quantum yield of unity obtained by the same authors with photographic plates illuminated by visible light remains constant only over a limited spectral region, probably

[47] *Z. Elektrochem.*, 20, 494 (1914).
[48] *J. Am. Chem. Soc.*, 37, 24 (1915); 38, 280 (1916).
[49] *Ibid.*, 48, 2603 (1926).
[50] *Ber. deutsch. physik. Ges.*, 1924, p. 23.

only so long as the energy of absorbed radiation quanta remains comparable to the work of transferring an electron from halide to silver ion in the crystal lattice of silver halides.

Further examples of chemical action of X-rays have been shown by Bordier,[51] who found that aqueous solutions of iodine and of starch-iodine are rapidly decolorised under their influence. It may be expected that systematic study will discover a considerable variety of other reactions stimulated by the action of X-rays.

Temperature and the Rate of Photochemical Reactions

At the beginning of the twentieth century, Goldberg[52] pointed to the characteristically small temperature coefficients of photochemical reactions as compared with those of thermal reactions. More recent investigations, although revealing the existence of photochemical reactions with comparatively large temperature coefficients, on the whole entirely support Goldberg's statement. Moreover, the original application of the quantum theory to photochemical reactions, which led to the postulation of the equivalence law, led also to the conclusion that the rate of photochemical reactions should be entirely independent of the temperature of the reacting body. Indeed, if the kinetic interpretation of the temperature coefficient of thermal reactions, an increased supply of activation energy to reacting molecules as the result of elevation of temperature, be accepted, then a special explanation for the existing influence of temperature on the rate of photochemical reactions will be required. For the activation energy in such reactions is supplied by a source of radiation independent of the temperature of the reaction system.

The first attempt to interpret the observed temperature coefficients was undertaken by Plotnikoff[53] who suggested a classification of all known data among three groups: to the first he assigned those averaging 1.04 for ten degrees temperature change, to the second those with values close to 1.2 and to the third those close to 1.4. In the opinion of Plotnikoff, the deviations of certain experimentally determined values from these averages are due to experimental errors. He suggested further that a definite temperature coefficient is an atomic property and remains unchanged in most photochemical reactions of a light sensitive atom.

In Tables 39, 40 and 41 are summarised the data now available on the temperature coefficients of photochemical reactions. Although this

[51] *Compt. rend.*, 163, 291 (1916).
[52] *Z. wiss. Phot.*, 4, 56 (1906).
[53] *Z. physik. Chem.*, 78, 573 (1911); also, "Lehrbuch."

TABLE 39. *Gasses.*

Reaction	Temperature Coefficient	Temperature Interval	Illumination [1]	Reference
$2HI \rightarrow H_2+I_2$	1.00	150–175°	Hg arc, quarz.	Bodenstein and Lieneweg, *Z.physik. Chem.*, **119**, 123 (1926).
$2NOCl \rightarrow 2NO+Cl_2$	1.00	0–78°	Incandescent lamp, glass	Kiss, *Rec. trav. chim.*, **42**, 665 (1923).
Photosensitisations by excited Hg atoms	1.00	25–70°	2536Å.	Marshall, *J. Phys. Chem.*, **30**, 1078 (1924).
$2Cl_2O \rightarrow 2Cl_2+O_2$	1.09	10–40°	Hg arc, glass	Kistiakowsky, *Z. phys. Chem.*, **116**, 371 (1925).
$2O_3+Cl_2 \rightarrow 3O_2+Cl_2$	1.17	16–25°	Hg arc, glass	Weigert, *Z. Elektroch.*, **14**, 591 (1908).
$2H_2+O_2 \rightarrow 2H_2O$	1.04	150–240°	Hg arc, quarz.	Coehn and Grote, *Nernst-Festschrift*, 136 (1912).
	1.06	131–228°	Hg arc, quarz.	Andrejeff, *J. Russ. Chem. Soc.*, **43**, 1342 (1911).
$2NH_3 \rightarrow 3H_2+N_2$	1.04	18–500°	2025–2140Å.	Kuhn, *Compt. rend.*, **178**, 708 (1924).
$3O_2 \rightarrow 2O_3$	1.00	−180–18°	<2000Å.	Eucken, *Z. physik. Chem.*, **107**, 436 (1923).
	<1.00 (low concentrations)			
$Cl_2+H_2 \rightarrow 2HCl$	1.21	11–60°	Sunlight	Bevan, *Proc. Cambr. Phil. Soc.*, **12**, 398 (1904).
	1.1		Incand. lamp, blue filter	Porter, Bardwell and Lind, *J. Am. Chem. Soc.*, **48**, 2603 (1926).
$Cl_2+SO_2 \rightarrow SO_2Cl_2$	0.88			Trautz, *Z. Elektrochem.*, **21**, 336 (1915).
$Cl_2+CO \rightarrow COCl_2$	1.00	18–28°	Incand. lamp, glass	Bodenstein, *Rec. trav. chim.*, **41**, 585 (1915).
	<1.00	18–350°	Incand. lamp, glass	Chapman and Gee, *J. Chem. Soc.*, **99**, 1726 (1911).
$2O_3 \rightarrow 3O_2$	1.15	18–35°	Hg arc, quarz.	Weigert, *Z. physik. Chem.*, **80**, 78 (1912)
	1.40		Incand. lamp, glass	Griffith and McKeown, *Trans. Far. Soc.*, **21**, 597 (1925).
	1.3 (high concentrations)			
	1.0 (low conc.)	0–20°	5800–6500Å.	Kistiakowsky. Unpublished.
$H_2+Br_2 \rightarrow 2HBr$	1.48	160–218°	Incand. lamp, glass	Bodenstein and Lütkemeyer, *Z. physik. Chem.*, **121**, 127 (1926).

[1] Unless the active spectral region has been defined by the author, in this column are given the source of light and the material of the reaction vessels, which, at least roughly, determine the range of active radiation frequencies.

TABLE 40. *Liquids.*

Reaction	Temperature Coefficient	Temperature Interval	Illumination	Reference
$C_2O_4H_2+UO_2^{\cdot\cdot}\rightarrow$ $\rightarrow CO_2+CO+H_2O+UO_2^{\cdot\cdot}$	1.00	4–80°	Sunlight	Bruner and Kozak, *Z. Elektrochem.*, **17**, 355 (1911).
	1.00	20–100°	Sunlight	Bacon, *The Philipp. J. of Sci.*, **5**, 281 (1910).
Lactic acid + $UO_2^{\cdot\cdot}$	1.00	20–30°	Carbon arc, glass	Bolin, *Z. physik. Chem.*, **87**, 490 (1914).
Quinine+CrO_4''	1.04	20–70°	Hg arc, thin glass	Goldberg, *Z wiss. Phot.*, **4**, 61 (1906).
Anthracene$\rightarrow$ $\rightarrow$Dianthracene	1.04	75–109°	Hg arc, glass	Weigert, *Ber.*, **42**, 854 (1909).
β-Methyl-anthracene$\rightarrow$ $\rightarrow$di-β-methyl-dianthracene	1.00	150–160°	Hg arc, glass	Weigert and Kruger, *Z. physik. Chem.*, **85**, 579 (1913).
$2Fe^{\cdot\cdot}+I_2\rightarrow$ $\rightarrow 2Fe^{\cdot\cdot\cdot}+2I'$	<1.17	25–35°	Incand. lamp, glass	Rideal and Williams, *J. Chem. Soc.*, **127**, 258 (1926).
$C_2O_4H_2+2FeCl_3\rightarrow$ $\rightarrow 2CO_2+2FeCl_2+2HCl$	1.02	3–44°	Sunlight	Lemoine, *Ann. chim. phys.*, **6**, 448 (1855).
	1.01	21–61°	Sunlight	Berthelot, *Compt. rend.*, **160**, 440 (1915).
Decomposition of lævulose	1.03	40–70°	Hg arc, quarz.	Berthelot. *Ibid.*
$NH_4Cr_2O_7+C_2H_5O$	1.00	20–30°		Plotnikoff, *Z. wiss. Phot.*, **19**, 40 (1919).
$2Co(C_2O_4)_3K_3\rightarrow$ $\rightarrow 2CoC_2O_4+3K_2C_2O_4+2CO_2$	1.06	12–22°	Incand. lamp, glass	Vranek, *Z. Elektrochem.*, **23**, 336 (1917).
$2HgCl_2+C_2O_4H_2\rightarrow$ $\rightarrow Hg_2Cl_2+2HCl+2CO_2$	1.19		Sunlight	Eder and Valenta, *Beitr. z. Photoch.*, **2**, 11 (1904).
Eder's solution	1.24		Sunlight	Eder, *Wien. Akad. Ber.*, 2 (1879).
$2H_2O_2\rightarrow 2H_2O+O_2$	1.50	21–45°	Hg arc uviol glass	Mathews and Curtiss, *J. Phys. Chem.*, **18**, 166 (1914).
	1.15	10–30°	Hg arc, quarz.	Tian, *Ann. phys.*, **5**, 248 (1916).
	1.32		Hg arc, quarz.	Kornfeld, *Z. wiss. Phot.*, **21**, 66 (1921).
	1.43	2–25°	Hg arc, quarz.	Anderson and Taylor, *J. Am. Chem. Soc.*, **45**, 1210 (1924).
$4HI+O_2\rightarrow 2H_2O+2I_2$	1.39	5–50°	Hg arc, glass	Plotnikoff, *Z. physik. Chem.*, **58**, 214 (1907).
$2CHI_3+2O_2\rightarrow$ $\rightarrow CO_2+CO+H_2O+3I_2$	1.42	3–51°	Hg arc, glass	Plotnikoff, *Z. physik. Chem.*, **75**, 337 (1910).

TABLE 40. *Liquids.—(Continued.)*

Reaction	Temperature Coefficient	Temperature Interval	Illumination	Reference
$2Cl_2+2H_2O \rightarrow 4HCl+O_2$	1.40	5–30°	Incand. lamp, glass	Benrath and Tuchel, *Z. wiss. Phot.*, **13**, 383 (1913).
$Cl_2+C_6H_6 \rightarrow$ $\rightarrow C_6H_5Cl+HCl$	1.50	6–20°	Sunlight	Slator, *Z. physik. Chem.*, **45**, 513 (1903).
$Br_2+C_6H_6 \rightarrow$ $\rightarrow C_6H_5Br+HBr$	1.40	6–19°	Hg arc, glass	Plotnikoff, *Z. physik. Chem.*, **78**, 579 (1912).
$Br_2+C_6H_5CH_3 \rightarrow$ $\rightarrow C_6H_5CH_2Br+HBr$	1.8		Sunlight	Bruner and Czernecki, *Bull. Ak. Sci. Crakow*, (A), 576 (1910).
$Br_2+K_2C_2O_4 \rightarrow$ $\rightarrow 2KBr+2CO_2$	1.98	0–15°	Incand. lamp, glass	Berthoud and Bellenot, *Helv. chim. Acta.*, **7**, 307 (1923).
$I_2+K_2C_2O_4 \rightarrow$ $\rightarrow 2KI+2CO_2$	3.22 3.15	25–40°	Incand. lamp: Red filter / Blue filter	Berthoud and Bellenot, *Helv. chim. Acta.*, **7**, 307 (1923).
Isomerisation of diethyl maleate ester	$(1.26)^{10}$ [a] $(1.02)^{10}$ [a]	21.5–24.5° 4–14°	4370–5570Å.	Wachholtz, *Z. physik. Chem.*, **125**, 1 (1927).
Bromination of the same	$(1.07)^{10}$ [a] $(1.02)^{10}$ [a]	21.5–24.5° 4–15°	4370–5570Å.	*Ibid.*

[a]). $\frac{k_{T+1}}{k_T}$

TABLE 41. *Solids.*

Reaction	Temperature Coefficient	Temperature Interval	Illumination	Reference
$AgBr \rightarrow 2Ag+Br_2$	1.03	–190–20°	Sunlight	Lumiere, *Compt. rend.*, **128**, 359 (1899).
	1.05	–85–15°	Sunlight	Padoa and Mervini, *Gazz. chim. ital.*, **47**, 288 (1917).
Bleaching of dyes in collodion films	1.04–1.07	15–80°	5700–6000Å.	Schwezoff, *Z. wiss. Phot.*, **9**, 65 (1910).
Phototropic changes:				
o-tolyl-piperyl--osazone	1.06	–90–10°		Padoa and Tabellini, *Gazz. chim. ital.*, **45**, 10 (1915).
p.p.-diamido-stilben-o-o-disulfonic acid	1.07	–10–20°		Padoa and Zazzaroni, *R. Acc. Linc.*, **24**, 828 (1915).
Benzaldehyde-phenylhydrazone	1.06	–80–0°		Padoa and Minganti, *R. Acc. Linc.*, **22**, 500 (1913).
Saliciliden-β-naphtyl-amine	1.40	0–10°		*Ibid.*
Styrol→Metastyrol	1.34	3–35°	Sunlight	Lemoine, *Compt. rend.* **129**, 717 (1899).

presentation is incomplete, the material gives sufficient evidence to permit the conclusion that neither the classification of the temperature coefficients among three groups, nor their constancy for the reactions of the same light sensitive atom is in accord with the actually observed relations.

Bodenstein [54] also attempted an interpretation of some relatively high temperature coefficients observed in such reactions as the bromination of toluene. Approaching the problem from a kinetic standpoint, he suggested that, for the success of a photochemical reaction, there is required not only the activation of the light absorbing component—this being independent of the temperature of the reacting body—but also, occasionally, an activation of the other reactant. The latter must be supplied by the energy of thermal agitation in a manner identical with that of thermal reactions, thereby producing the sensitivity of the photochemical reaction to temperature changes. It follows from this that the temperature coefficient of the completely thermal reaction must be higher than that of the photochemical since, in such case, the activations of both reactants have their origin in the supply of thermal energy.

Tolman's Theory of Temperature Coefficient. A new aspect of the problem was brought forward by the theoretical treatment of the temperature coefficients of photochemical reactions by Tolman.[55] The starting point of his development is the consideration that molecules of a system are in different internal quantum states at a given temperature of the reacting body and that the probability that a molecule will absorb radiation energy of the frequency ν and will subsequently react depends not only on the density of radiation but also on the original quantum state of the molecule. The distribution of N molecules in a system among different quantum states is given, according to Tolman, by the expression

$$N_i = N \frac{p_i e^{-\epsilon_i/kT}}{\Sigma p_i e^{-\epsilon_i/kT}}$$

which corresponds exactly with the classical Maxwell-Boltzmann distribution law. Here N_i is the number of molecules in the i-th quantum state, ε_i the corresponding energy content, p_i the a-priori probability [56] of the i-th quantum state; k, Boltzmann's constant and T, the absolute temperature. The summation in the denominator is

[54] *Z. physik. Chem.*, 85, 380 (1913).
[55] *J. Am. Chem. Soc.*, 42, 2506 (1920); 45, 2285 (1923); comp. also Pratalongo, *Gazz. chim. ital.*, 48, 121 (1918).
[56] Usually a magnitude not far from unity.

extended over all possible quantum states of the molecules of a given system. Assuming further that $a_{i\nu}$ and $s_{i\nu}$ are the probabilities for a molecule in the i-th quantum state to absorb radiation energy of the frequency ν and to react subsequently, Tolman arrives at an expression for the temperature coefficient of a unimolecular photochemical reaction proceeding under the influence of monochromatic radiation of a constant density throughout the reacting body, that is to say with only slight absorption:

$$\frac{d\ln k_\nu}{dT} = \frac{1}{k_\nu}\frac{\sum_0^\infty \alpha_{i\nu}s_{i\nu}p_i e^{-\epsilon_i/kT}\cdot\frac{\epsilon_i}{kT^2}}{\sum_0^\infty p_i e^{-\epsilon_i/kT}} - \frac{\sum_0^\infty p_i e^{-\epsilon_i/kT}\cdot\frac{\epsilon_i}{kT^2}}{\sum_0^\infty p_i e^{-\epsilon_i/kT}}$$

which can be written [57]

$$\frac{d\ln k_\nu}{dT} = \frac{\bar{\bar{\epsilon}} - \bar{\epsilon}}{kT^2}$$

In this expression $\bar{\bar{\epsilon}}$ is the average energy of the molecules which pick up radiant energy and react and $\bar{\epsilon}$ is the average energy of all the molecules. In a similar manner, for a bimolecular reaction, Tolman derives the expression:

$$\frac{d\ln k_\nu}{dT} = \frac{1}{2T} + \frac{\bar{\bar{\epsilon}}_a - \bar{\epsilon}_a + \bar{\bar{\epsilon}}_b - \bar{\epsilon}_b}{kT^2}$$

in which the negligibly small term $\frac{1}{2T}$ is due to an increase of collision frequency with temperature increase, $\bar{\bar{\epsilon}}_A - \bar{\epsilon}_A$ has the same meaning as in the expression for the unimolecular reactions and $\bar{\bar{\epsilon}}_B - \bar{\epsilon}_B$ is the difference between the average energy of those molecules of the kind B which enter into reaction with activated molecules A and the average energy of all the molecules of B. For a bimolecular reaction, Tolman thus arrives at the conclusion, already reached by Bodenstein, that not only the light absorbing molecules, but also other reactants may need activation for successful reaction. The term $\bar{\bar{\epsilon}}_A - \bar{\epsilon}_A$ in the equation for a bimolecular reaction and the entire expression for the uni-

[57] Of practical convenience for the calculation of logarithmic temperature coefficients from the value $\frac{k_{T+10}}{k_T}$ more frequently employed, is the approximate relation between these two ways of expressing the same magnitude: $\frac{d\ln k}{dT} = \frac{1}{5}\left(\frac{r-1}{r+1}\right)$ where $r = \frac{k_{T+10}}{k_T}$. This relation was deduced by Tolman.

molecular reactions are entirely new and of considerable theoretical interest. If an average molecule has the same chance of absorbing light and reacting as one in a higher quantum state, then, of course, the energies $\bar{\varepsilon}$ and $\bar{\varepsilon}$ must be equal and the logarithmic temperature coefficient will be zero. The ordinary coefficient $\frac{k_{T+10}}{k_T}$ is equal to unity under these circumstances. Among the reactions cited in Tables 39, 40 and 41, a considerable number will be found which very closely approximate to this simplest case. It is undoubtedly significant that those reactions which have a constant integral quantum yield not far from unity are particularly numerously represented in this group. For a discussion of the rest of the experimental material, Tolman's interpretation of the meaning of the term $\bar{\varepsilon} - \bar{\varepsilon}$ in his expression needs further definition.

Let us consider first the case in which the probability of a reaction on absorption of radiation energy is essentially independent of the quantum state of light absorbing molecules prior to light absorption. The energy $\bar{\varepsilon}$ becomes then the average energy of all those molecules in the system which can absorb radiation of a given frequency. It will be immediately seen that, in this case, the temperature coefficient of the reaction rate is reduced to the temperature coefficient of the light absorption coefficient, or, in other words, the reaction rate per unit of energy absorbed is independent of the temperature. In extreme cases, when the probability of reaction on activation ($s_{1,\nu}$) is near to unity, the reactions of this type must follow the equivalence law; otherwise, a certain additional temperature coefficient of the reaction rate due to temperature influence on the reaction probability would be expected. Tolman suggests, however, that such variations are small. In the case of bimolecular reactions, finally, the temperature coefficient may be caused by the second term ($\bar{\varepsilon}_B - \bar{\varepsilon}_B$) of Tolman's equation.

The experimental data gathered in Tables 39 to 41 give of themselves no decisive answer as to the applicability of this specialised form of Tolman's equation, since, in all these determinations of the temperature coefficients, the light absorption, if measured at all, has been measured only at one temperature. The fact, however, that several of the reactions cited have been studied under conditions of total light absorption by the reactant, that is, with light absorption which could not possibly be altered by temperature changes of the reacting body, shows definitely that the temperature variation of light absorp-

tion alone cannot account for the observed temperature coefficients of photochemical reactions. Still, this factor may be of a considerable importance, since an influence of molecular light absorption through temperature changes has very frequently been observed. The effect of temperature increase consists usually in a broadening of the absorption bands, increase of absorption being particularly pronounced on the long wave side of the original band. A detailed discussion of the ample experimental material on the subject lies outside the scope of the present book; attention will, therefore, be directed only to data on the behaviour of a few gases that are particularly interesting in the study of photochemistry.

Light Absorption and Temperature. As Wartenberg [58] has found, the absorption of oxygen molecules in the ultraviolet extends, at 1800° from shorter wave lengths to 3000 Å. A comparison with the absorption region of oxygen molecules at room temperature (<2000 Å.) shows that, in this case, the light absorption coefficients, at least in the spectral region 2000-3000 Å., must be considerably increased by increase of temperature. In all probability, the influence of temperature is larger for longer waves. In this connection it is of interest to note the equation which results, as Tolman pointed out, from differentiating his expression for the temperature coefficients with respect to the frequency of active radiation. For both the uni- and the bimolecular reactions, this operation yields the same expression:

$$\frac{d}{d\nu}\left(\frac{d\ ln\ k^{\nu}}{dT}\right) = \frac{1}{kT^2}\frac{d\bar{\epsilon}}{d\nu}$$

Combining this equation with the data on oxygen, the conclusion can be reached that the absorption in the longer wave spectral region is due to molecules which have already a considerable amount of internal energy; further, it is probable that the longer the wave length, the larger the average internal energy of the light absorbing molecules. This conclusion is not limited to oxygen and can be extended to other substances, if similar relations in their absorption spectra are found.

It might be suggested on the basis of this conclusion that, in the photochemical ozonisation experiments of Warburg, the internal energy of the light absorbing oxygen molecules supplied the difference between the energy of the absorbed quanta and the energy required for the dissociation process. A brief calculation shows, however, that for light of the wave length 2070 Å. the internal energy should be of the order of 30,000 cal., and for light of the wave length 2530 Å. as

[58] *Physik. Z.*, **11**, 1168 (1910).

much as 50,000 cal. Concentrations of molecules with such internal energies are vanishingly small at room temperature. Moreover, the temperature coefficients of light absorption should then have, for these wave lengths, the impossibly high values of 5 and 25 for 10° temperature change. Still, the fact that in a definite spectral region only molecules with internal energies considerably larger than the average absorb radiation, partly explains the absence of that sharp photochemical threshold which was to be expected on the basis of the equivalence law.

The influence of temperature on the light absorption of bromine has been investigated by Ribaud.[59] He finds that, in the region of maximal (continuous) absorption (4210 Å.), an increase of temperature by 600° slightly decreases the light absorption coefficients. On both sides of the maximum the coefficients are markedly (2-fold and more) increased by this change of temperature. An extension of chlorine absorption towards longer wave lengths at higher temperature has been observed by Dobbie and Fox.[60] Later, Kuhn [61] studied the influence of temperature on absorption in the region of the band absorption spectrum around 5000 Å. It can be calculated from his data that the temperature coefficient of light absorption in this spectral region is 1.12 at room temperature. By analogy with bromine it may be concluded that, in spectral regions of shorter wave length, the temperature coefficients are smaller (comp. Kuhn, *loc. cit.*). In good qualitative agreement with these observations on the temperature influence of the light absorption are the measurements of temperature coefficients of varied photochemical reactions, in their relation to the wave length of active radiation. These have been carried out mainly by Padoa and his co-workers. The data are summarised in Table 42. The agreement obtained is, however, only qualitatively good, as a comparison of the data on the hydrogen-chlorine reaction with those on light absorption by chlorine will immediately show. The temperature coefficients of the photochemical reaction are apparently, throughout the spectral region investigated, considerably larger than those of the light absorption. Such a conclusion is not limited to the hydrogen-chlorine reaction but can be similarly applied to other photochemical reactions of chlorine, as also to the majority of the experimental material presented in Tables 39 to 41. Obviously, the variations in light absorption with temperature cannot account

[59] *Ann. Physique*, 12, 107 (1919).
[60] *Proc. Roy. Soc.*, A 99, 456 (1921).
[61] *Z. Physik*, 39, 77 (1926).

TABLE 42.

I

$Cl_2 + H_2 \rightarrow 2HCl$ [a] 10°–40°

Spectral region	ultra violet	violet	blue	green
$\frac{k_{T+10}}{k_T}$	1.17	1.21	1.31	1.50
Activation energy	2800	3300	4800	7200 cal.

II

Eder's solution [b] 20°–40°

Spectral region	2800–4000	4480 Å	green (sensitised by tetrabromofluorescein)
$\frac{k_{T+10}}{k_T}$	1.05	1.21	1.75
Activation energy	900	3300	10,000 cal.

III

Oxidation of HI in aqueous solution [c]

Spectral region	4200–4800	4800–5670	6070–7220 Å.
$\frac{k_{T+10}}{k_T}$	1.85	1.20	1.07
Activation energy	7500	3300	950 cal.

IV

Photographic papers (silver citrate)[d]; -85°–+15°

Spectral region	ultra violet,	blue
$\frac{k_{T+10}}{k_T}$	1.07	1.119
Activation energy	1000	2900 cal.

V

Photographic plates, sensitised by pinachrom [e]

Spectral region	4360	5460–5790 Å.
$\frac{k_{T+10}}{k_T}$	1.07	1.08

VI

Phototropic change of saliziden-β-naphthylamine [f]

Spectral region	violet	blue	green
$\frac{k_{T+10}}{k_T}$	1.39	1.45	1.8

[a] *Atti accad. Lincei*, 25 II, 215 (1916).
[b] *Atti accad. Lincei*, 24 II, 97 (1915).
[c] *Gazz. chim. ital.*, 55, 87 (1925).
[d] *Atti accad. Lincei*, 25 II, 168 (1916).
[e] Daletzki, comp. Plotnikoff, "Lehrbuch."
[f] *Atti accad. Lincei*, 24, 828 (1915).

completely for the temperature coefficients of photochemical reactions, not even for their dependence on the frequency of active radiation.

In order better to reconcile the experimental material with the conclusions drawn from Tolman's expression it is necessary to consider that all of the photochemical reactions enumerated are not unimolecular and that, for bimolecular reactions, Tolman predicts the possibility of temperature coefficients due to activation energy of the non-absorbing component, as also to variations in collision frequency. For other than gaseous reactions, these are not necessarily represented by a $\sqrt{T_{abs.}}$ function. A detailed discussion of the factors causing temperature coefficients of the rates of these more complicated reactions will be postponed until the end of this chapter.

Unfortunately for the practical importance of Tolman's equation for unimolecular reactions, no such simple reactions have been observed so far. In all known cases the primary—unimolecular—process is followed by a sequence of secondary reactions. Only their totality is accessible to observations and the isolation of the temperature coefficient coming from the primary process would be somewhat arbitrary.

Photodecomposition of Ammonia. Even those reactions which outwardly have the characteristics of unimolecular reactions, as, for instance, the proportionality of the reaction rate to the absorbed light energy and the independence of the rate from the concentrations of the reactant and of diluents, consist in reality of a sequence of intermediary processes. A particularly typical example of a reaction, which, only by means of a more exhaustive study, has been shown to possess complicated kinetics, is the decomposition of ammonia. This reaction is of particular interest in this section since it is the only one for which the reaction rate and the light absorption have been measured over a wide range of temperatures.

Ammonia shows a marked absorption of light only in the far ultraviolet. According to Leifson[62] it has a system of bands below 2260 Å.

Warburg[63] was the first to investigate the kinetics of the photochemical reaction. Warburg concluded that, in the absence of oxygen, the reaction on illumination of ammonia is a decomposition into nitrogen and hydrogen according to the stoichiometric equation:

$$2NH_3 \rightarrow N_2 + 3H_2.$$

For his experiments, carried out at room temperature, Warburg used

[62] *Astrophys. J.*, **63**, 73 (1926).
[63] *Sitzb. Preuss. Akad.*, 746 (1911); 216 (1912).

approximately monochromatic light of 2025-2140 Å. wave length and studied the influence on the rate of reaction of the concentration of ammonia in a mixture with hydrogen and nitrogen. He found the quantum yield of the decomposition to be less than unity, 0.25, unchanged by variations of ammonia concentration or by addition of larger amounts of a mixture of hydrogen and introgen in the stoichiometric proportion of 3:1. The reaction is thus not retarded by its decomposition products and no stationary state is being formed on prolonged illumination. This latter conclusion was confirmed by Coehn and Pringent.[64] Kuhn [65] obtained essentially similar results on the course of the reaction. The quantum yield was found to be independent of the ammonia pressure within wide limits (5 to 300 mm.) and an exact doubling of the gas pressure was obtained on total decomposition of a sample of ammonia. The rate of reaction was further found to be proportional to the incident light intensity. The absolute value of the quantum yield, as found by Kuhn, differs considerably, however, from the value of Warburg. Kuhn further reported that, by increasing the monochromatic nature of the radiation, using, instead of a group of zinc lines between 2025-2140 Å., only two lines, 2063 and 2100 Å.—the quantum yield can be decreased from 0.45 to 0.10. Of particular interest is the observation of Kuhn that the quantum yield of ammonia decomposition is not independent of temperature but increases by about 50 per cent for every 100° temperature increase, reaching a 7-fold value (3.3) at 500°. Unless a considerable error is involved in Kuhn's measurements, this increase, being independent of the absolute temperature, represents a class of temperature coefficients which do not obey the Arrhenius equation. According to Kuhn, the kinetics of the reaction are changed at high temperatures, hydrogen, but not nitrogen, under these conditions showing a strong retarding action on the rate of reaction. Kuhn advanced a theory of the reaction mechanism which implies that only a part of the ammonia molecules which absorbed light energy decompose. The primary photochemical process is assumed to be a unimolecular decomposition:

$$NH_3 \rightarrow N + H + H_2.$$

A sequence of secondary processes is expected by him to account for the observed variations in the quantum yield. As Bates and Taylor [66] recently pointed out, a primary process of the type suggested by Kuhn is impossible according to the recent data on the heats of dissociation

[64] *Z. Elektrochem.*, 20, 275 (1914).
[65] *Compt. rend.*, 178, 708 (1924); 177, 956 (1923); *J. chim. phys.*, 23, 521 (1926).
[66] *J. Am. Chem. Soc.*, 49, 2438 (1927).

of nitrogen and of hydrogen molecules, since it requires about 60,000 cal. more than is supplied by the absorbed quanta. Bates advanced a theory of the reaction mechanism based mainly on his observations [67] that ammonia can be decomposed even by excited mercury atoms with an energy content of only 112,000 cal. and that the gaseous reaction products are not in the stoichiometric ratio $1N_2:3H_2$ but contain considerably more hydrogen. Bates suggests that all ammonia molecules are decomposed on light absorption, either in a bimolecular reaction:

$$(1)\quad NH_3' + NH_3 \rightarrow N_2H_4 + H_2$$

or unimolecularly:

$$(2)\quad NH_3' \rightarrow NH_2 + H.$$

The following secondary reactions can also take place:

$$(3)\quad H + H \rightarrow H_2$$
$$(4)\quad NH_2 + NH_3 \rightarrow N_2H_4 + H$$
$$(5)\quad NH_2 + H_2 \rightarrow NH_3 + H.$$

As a whole, on these assumptions, the reaction leads to the formation of hydrazine and of hydrogen, which process does not involve any change in the number of gas molecules. Therefore, Warburg and Kuhn, who both used a manometric method, would not be following this reaction but would be measuring the rate of secondary hydrazine decomposition. At room temperature hydrazine is probably only decomposed photochemically, but, at higher temperatures, a thermal reaction may take place. This would then partly account for the increase of the "apparent" quantum yield obtained by Kuhn. The deficiency of the quantum yield at low temperatures would be due mainly to the reversal of reaction (4). The retardation by hydrogen at higher temperatures would be caused by reaction (5) which must be very slow at room temperature since no retardation by hydrogen was observed by Warburg. This reaction mechanism is undoubtedly more plausible than that postulated by Kuhn. Still it meets great difficulties in accounting for several observations of Warburg and of Kuhn. The facts that neither of them observed an "induction period" of pressure increase on illumination [68] and that, on total decomposition, a doubling of the pressure in a smooth curve was obtained, indicate, of course, that the stationary concentration of hydrazine in illuminated ammonia is very small. Since, in the stationary state, the rate of hydrazine formation must be equal to the rate of its decomposition and this latter is essentially photochemical

[67] Comp. page 133.
[68] No relation between the apparent quantum yield and the actually observed pressure increase can be detected in the data of Kuhn.

at room temperature, hydrazine should have an extraordinarily high light absorption coefficient in the spectral region studied by Warburg and by Kuhn. It may be pointed out that Bates could not detect any change in the absorption spectrum of ammonia on longer illumination. The reversal of reaction (4) can only lead to a decrease in the rate of hydrazine formation when combined with reaction (5). We have seen, however, that, at room temperature, hydrogen has practically no retarding effect on the rate of integral reaction. The reaction $NH_2 + H \rightarrow NH_3$, which might be suggested, cannot play an important rôle in the reaction mechanism, since, otherwise, the rate of reaction would be proportional, not to the incident light intensity as was found by Kuhn, but to the square root of it. Finally, the quantum yield at high temperatures increases considerably above the limiting value of 2.0 deduced by Bates from his mechanism. All these discrepancies indicate that either the earlier observations are partly erroneous or that the mechanism postulated by Bates must be considerably modified. The point which is unquestionably established by the more recent studies on ammonia decomposition is that the mechanism of this reaction, although apparently so simple at room temperature, is in reality quite complicated. It is therefore not astonishing that the reaction shows a deviation from the course prescribed by Tolman for unimolecular reactions; its quantum yield, instead of remaining constant, increases with temperature. To assume that the probability of reaction of activated molecules increases rapidly with temperature would hardly help in our difficulty since the observed quantum yield increases well beyond the value of unity. Obviously, a kinetic interpretation of the temperature coefficient of ammonia decomposition necessitates consideration of factors additional to those which were included by Tolman in his theoretical discussion of the two simplest ideal cases of photochemical kinetics.

Relation between influences of the frequency of radiation and of the temperature on the quantum yield. Attention may be now turned to another meaning which can be attributed to Tolman's equation:

$$\frac{d \ln k_\nu}{dT} = \frac{\bar{\bar{\epsilon}} - \bar{\epsilon}}{kT^2}$$

It is consistent with the assumptions made by Tolman in deriving this equation that the term $\bar{\bar{\epsilon}}$ be regarded as the average energy of only a fraction of the molecules absorbing light of a given frequency, namely of those which can react afterwards. It is thereby assumed that molecules in several different quantum states can absorb the

same radiation frequency and that their subsequent reactivity is dependent on their original energy content. It is of course doubtful whether such "different" molecules can all absorb the same monochromatic radiation. We are going to deal, however, with photochemical reactions in solutions where the action of neighbouring molecules causes a far-reaching, broadening and partial overlapping of single absorption bands; it must be further remembered that practically no photochemical reactions have ever been studied in strictly monochromatic light, radiation of somewhat wide spectral widths being always used.

According to our present interpretation, the temperature coefficient of a photochemical reaction is not equal to the temperature coefficient of light absorption but may be much larger (this case is the only one of practical interest), if among the molecules absorbing light in a spectral region only those with highest original quantum energy are activated for reaction by absorption of light quanta. Further, even if the reaction probability of these particularly activated molecules is nearly unity, the measured reaction cannot have a quantum yield close to unity since a part of the light energy is absorbed by those molecules which do not become chemically activated on account of their lower original quantum energy. It must rather be concluded that, unless a chain mechanism is set up by the primary photochemical process, the quantum yield will be considerably smaller than unity. The field of application of Tolman's equation as thus specified is obviously very limited. At the same time, it directs attention to reactions where large deficiencies of the quantum yield have been observed and in particular to those which show a decrease of the quantum yield with frequency of radiation. It was pointed out earlier that, as one of the possible causes of the decrease of the quantum yield, a screening action of that portion of the reactant molecules which does not become chemically activated on light absorption may be suggested. Such being the case, we may expect that the smaller the absorbed radiation quanta, the larger must be the internal energy of molecules to obtain a chemical activation. A test of these suggestions is now offered by Tolman's equation since, if they are correct, larger temperature coefficients of reaction rates should be found in light of higher wave length. Unfortunately no experimental material is available on such typical reactions as the decompositions of oxalic acid and of the chloroplatinic acids. Nothing can be said at present definitively as to the magnitude of the expected effects, since a simple calculation with the data of Table 42 shows that the sum of the energy of the absorbed radiation quanta and the internal activation energy

as calculated from the temperature coefficients does not remain substantially constant over wide spectral regions, but, on the contrary, decreases with frequency of radiation.

So far, attention was concentrated on the temperature coefficients of photochemical reactions as caused by the light absorbing reactants. It was made obvious that, although a far-reaching parallelism exists between the temperature coefficients of the reaction rate and of the light absorption, nevertheless the variations in the latter cannot quantitatively account for the variations of the former. Those reactions which have small temperature coefficients, not exceeding 1.05-1.08, constitute a possible exception to this conclusion. For a group of photochemical reactions with quantum yields dependent on the wave length of absorbed radiation and usually small, the suggestion was advanced that only a part of the light-absorbing molecules, namely those with large internal energies,[69] can be chemically activated on absorption of light energy.

Inelastic collisions as a cause of temperature coefficients. In order to simplify his calculations, Tolman considered only two possible fates for an activated molecule, a chemical reaction and a re-emission of absorbed energy as fluorescence radiation. The reaction probability for molecules in a given quantum state was further assumed by him to be essentially independent of temperature.

The developments of the earlier chapters have frequently shown the importance of a third process involving activated molecules: the degradation of energy by inelastic collisions. Very little is actually known as to the relation of the yield of inelastic collisions to the temperature of the body. Franck [70] suggested, on the basis of qualitative experiments, that the frequency of such collisions between mercury atoms and nitrogen molecules is considerably decreased at higher temperatures. More recently, however, Cario and Franck [71] have interpreted the effect differently. They show that inelastic collisions between mercury and nitrogen do not lead to a complete loss of the excitation energy by the former, but only to the loss of a small fraction of it, the quantum state of the mercury atom being changed from 2^3P_2 to 2^3P_3 and the energy content being decreased by *circa* 4600 cal. per mol. In this new quantum state, the mercury atoms are in a metastable condition and have a life sufficiently long to enable them to collide with some impurities of the gasses (H_2, CO, etc.) or with the

[69] It is, however, not excluded that the kinetic energy of activated molecules also has a bearing on their reactivity.
[70] *Naturwiss.*, 14, 211 (1926).
[71] *Z. Physik*, 37, 613 (1927).

walls of the vessel and thereby lose the remainder of the activation energy before the emission of fluorescence can occur. At higher temperatures, however, an increasing number of collisions between metastable mercury atoms and energy rich introgen molecules, collisions of the first kind, begin to take place, resulting in a transfer of energy to the atoms, thus raising them back into the 2^3P_2 quantum state and making possible the emission of resonance fluorescence. Cario and Franck pointed out, however, that their observations do not deny the validity of Franck's original suggestion: that is, that a negative temperature coefficient of the yield of inelastic collisions may still exist, since the probability of a collision being inelastic must depend on the relative velocity of colliding atoms. A temperature coefficient is even more likely in the case of excited molecules on account of rotational and vibrational quantum states, which are determined mainly by the temperature of the body and which may affect considerably the stability of excited molecules to inelastic collisions. To this factor may eventually be attributed the variations in the temperature coefficient of ozone decomposition, for which a value of 1.34 was obtained at higher gaseous concentrations and a much smaller value (less than 1.1), at concentrations sufficiently low to exclude inelastic collisions as the determining factor of the reaction mechanism.[72]

Secondary reactions as the cause of temperature coefficients. Bodenstein, and particularly Tolman, suggested that the thermal activation of the non-absorbing component of a bimolecular photochemical reaction may sometimes cause the large temperature coefficients of these processes. Undoubtedly this factor is of considerable importance; but, on the other hand, a more detailed kinetic study of apparent uni- or bimolecular photochemical processes has usually revealed the existence of secondary reactions of a more or less complicated character. It would be incorrect under these circumstances to speak of the activation energy of the non-absorbing reactant as the sole origin of the temperature coefficient. Rather, it should be suggested that the totality of these secondary reactions which follow the primary photochemical process is the true origin of the temperature coefficients. Returning once more to the reaction of bromine and hydrogen we see that the integral reaction velocity is determined mainly by the rates of two competitive processes:

$$Br + H_2 \rightarrow HBr + H$$

and

$$Br + Br \rightarrow Br_2.$$

The first requires a considerable activation energy and is therefore

[72] Comp. page 170.

rapidly accelerated by temperature increase; the rate of the second is probably determined by the collision frequency and hence is proportional to the square root of the absolute temperature. The result is a considerable temperature coefficient of the integral reaction velocity. The relations observed in the reactions of iodine and bromine with potassium oxalate in aqueous solution are very similar, although here the rate of formation of halogen molecules from the atoms may be influenced considerably more by temperature than is suggested by a $\sqrt{T_{abs.}}$ function. According to Porter, Bardwell and Lind [73] the relatively high temperature coefficients observed by Padoa and by others in the hydrogen chlorine reaction are due to a specific destruction of an inhibitor action at higher temperatures. If this effect is eliminated, a value below 1.1 results under experimental conditions, excluding large variations of light absorption with temperature. To a somewhat similar cause should be attributed those rather unusual temperature coefficients smaller than unity. They can hardly be ascribed to the reacting molecules being those whose energy is smaller than the average; such an assumption is rather improbable a priori; and furthermore, since the average energy of molecules at lower temperatures is small, even if the reacting molecules had no energy at all prior to light absorption, the resulting temperature coefficient would still be hardly different from unity.[74] Such temperature coefficients should rather be interpreted as definitely indicating the presence in the chain mechanism of a retarding process whose activation energy, and therefore temperature coefficient, is higher than those competing reactions which lengthen the chains; the net combined result of these two opposing actions is a decrease in reaction rate with temperature increase. Such competition of two or more secondary processes with their specific rates and necessary activation energies, which determines the length of chains and, therefore, the integral reaction velocity, determines also the temperature coefficient. These processes being identical in nature with thermal reactions, it is only natural to expect that their activation energies and therefore the temperature coefficients will be of the same order of magnitude.

[73] *J. Am. Chem. Soc.*, 48, 2603 (1926)
[74] See Tolman, *loc. cit.*

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By J. M. Weiss, C. R. Downs and Dorothy A. Hahn.

Measurement of Particle Size and Its Application
By L. T. Work.