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THE PHOTOCHEMICAL
EFFICIENCY OF THE ABSORBED
RADIATION

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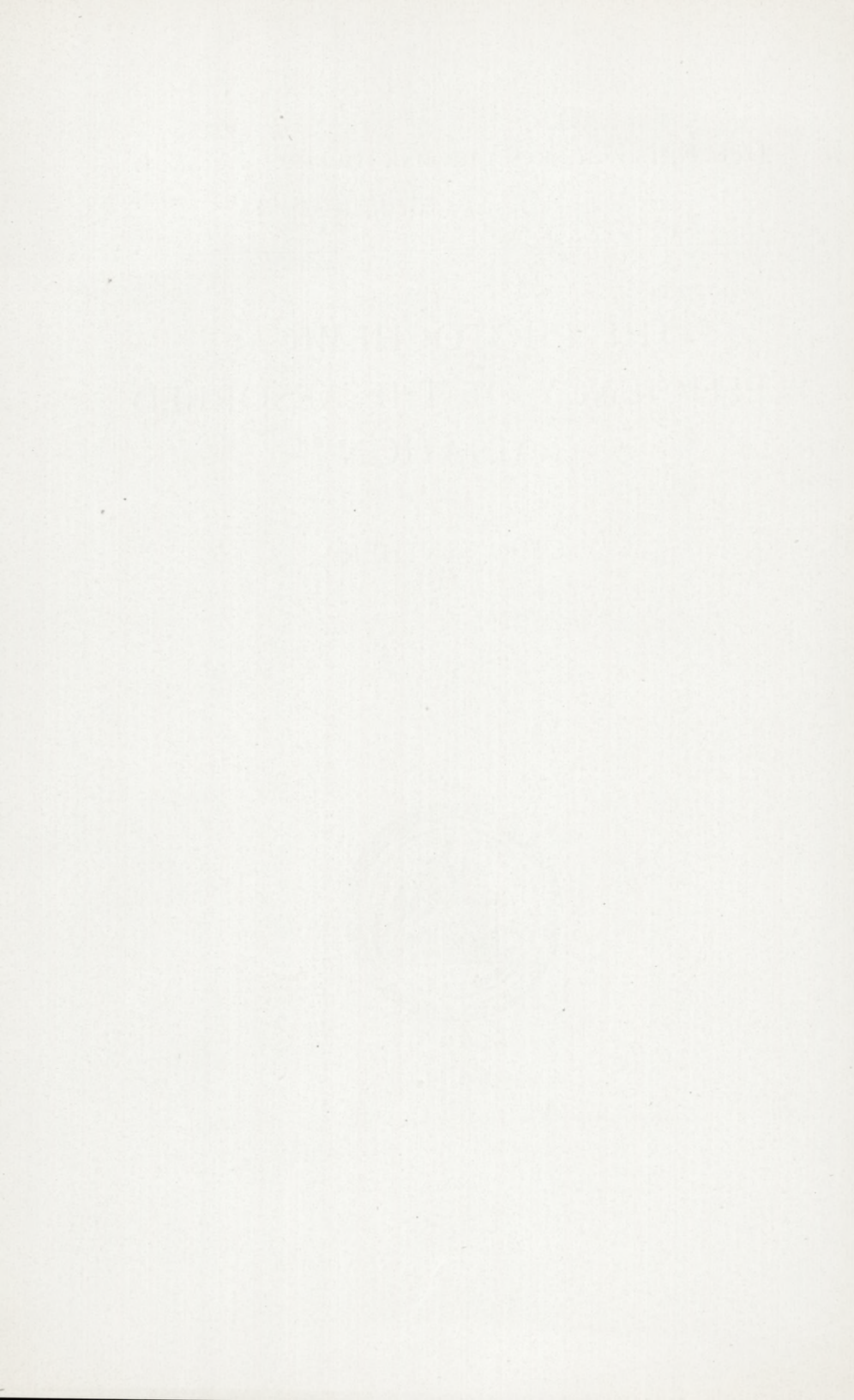
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I. The Efficiency of the Absorbed Radiation.

GENERALLY speaking the absorbed radiation will — perhaps through several intermediate links — finally be transformed to thermal energy. In those cases in which a chemical process takes place in the absorbing system in consequence of the absorption, part of the absorbed radiation must, — as has long been known¹ — at any rate provisionally, be transformed to chemical energy. One of the most important problems in modern photochemistry has accordingly been, to find relations between the absorbed amount of energy and the chemical change produced hereby, in other words, to find a regularity in the numerical expressions for the light-sensitiveness which apparently reaches from very great to very small values. The task may be still more accurately defined.

It has long been customary, according to HELMHOLTZ'² example, to divide the photochemical processes into reversible or work-accumulating and irreversible or work-yielding, after the analogy of the division of the darkness-processes. This division is, as far I can see, erroneous, as it does not at all touch upon the actual photochemical part of the total light-process, which must in all cases be considered as complex. This actual photo-

¹ OSTWALD, Lehrb. d. allgem. Chemie II, 1, 1087.

² Erhaltung d. Kraft 25 (1847).

chemical division-process, the primary photochemical process, consists — like ordinary light-absorption — in an absorption of radiation-energy, i. e. in an augmentation of the chemical potential of the absorbing substance. After this follows one or more, necessarily voluntary, secondary darkness processes which, hence, occur with loss of free energy. These two processes being quite independent of each other, it is evidently quite indifferent to the primary process whether this secondary loss of free energy is greater or smaller than the primary augmentation of the same. In the first case we have an irreversible, in the second a reversible total light-process, and the argument shows that, with regard to the photochemical part of the process, there is no difference between the two groups. For the total process the difference does not arise until the moment when the reverse reaction in the reversible process under the given circumstances has a measurable velocity.

Photochemical statics and dynamics render us several examples of the correctness of this reasoning.

As an example WARBURG¹, REGENER² and COEHN³ have examined the decomposition of ammonia into nitrogen and hydrogen at ultra-violet insolation. By combining the observations of these investigators the velocity of decomposition proves constant until the decomposition is complete. At ordinary temperature and pressure in darkness the equilibrium lies at abt. 1,5 per cent decomposition. If pure ammonia, there, be exposed, the radiation acts in the same direction as the chemical forces in the first

¹ Sitzungsber. d. Berliner-Akad. 1911, 746.

² Sitzungsber. d. Berliner-Akad. 1904, 1228, *Drud. Ann.* 20, 1033 (1906).

³ *Jahrb. Rad. Elektr.* 7. 615 (1910), *Zeitschr. f. Elektroch.* 20, 275 (1914).

$1\frac{1}{2}$ per cent decomposition, the process is, consequently, irreversible. As soon as we reach the $1\frac{1}{2}$ per cent decomposition, the process becomes an equilibrium displacement, hence reversible, without the velocity in any way being affected thereby. The fact that the decomposition can here be complete is partly due to the circumstance that the reverse process, the formation of ammonia, has no measurable velocity at ordinary temperature, partly to its lack of sensitiveness to the radiation employed.

Quite similarly COEHN and BECKER¹ have been able to displace the equilibrium $SO_2 + O \rightleftharpoons SO_3$ at ultra-violet insolation without it having been noticeable in the velocity when the darkness-equilibrium was passed. When here only a SO_3 decomposition of 35 per cent was reached, in spite of the darkness-velocity of the process under the given circumstances being exceedingly slight, it is due to the fact, that both processes are here sensitive to the employed, mixed radiation, and that the obtained stationary state consequently depends upon the spectral composition of the radiation.

As a third example may be named the process $HgCl_2 + FeCl_2 \rightleftharpoons HgCl + FeCl_3$ which I have previously² investigated. When the left hand system was exposed in the presence of oxygen, a general oxidation of the ferro-salt to basic ferri-salt simultaneously took place, which process is sensitive to the same spectral region as the first named, so that in both cases it is undoubtedly the ferro-salt, which is the actual sensitive substance. The distribution of ferro-salt between these two processes is now exclusively dependent on the ratio between the amounts of mercury-

¹ Zeitschr. f. physikal. Chemie. 70, 88 (1909).

² Overs. o. d. kgl. danske Vid. Selsk. Forh. 1911, Nr. 5.

salt and oxygen, and of the velocity by which exposed ferro-salt reacts with these substances, but without regard to the fact of the one process being reversible, the other irreversible.

Finally we shall mention that LUTHER and WEIGERT¹ by exposure of anthracene-solution formed measurable quantities of dianthracene, which was in inverse proportion to the velocity of the opposite transformation, and that WEIGERT² at 500° was unable to obtain any displacement at all of the equilibrium $COCl_2 \rightleftharpoons CO + Cl_2$, despite the fact of both the reverse processes being sensitive. The cause is that both processes at the high temperature occur too rapidly for the light to compete with it.

These examples, to which several others could be added, show, conformably to the above reasoning, that the effect of the exposure is not at all dependent upon the magnitude and direction of the affinity in the total process, but that, in the so-called reversible light-processes, the question is solely of a competition between the light-effect and the velocity of the reverse process.

In spite of this, it will be practical provisionally to keep to the above division also here.

For the reversible processes, in which the total light-effect consists in an augmentation of free energy, it will be natural to compare this augmentation of energy with the absorbed energy of radiation which has had to be employed in order to produce it. In this manner several investigators, amongst whom especially WEIGERT³, have computed the efficiency for various reversible processes and

¹ Zeitschr. f. physikal. Chemie 51, 297. 53, 385 (1905).

² Ann. d. Physik (4) 24, 55 (1907).

³ Zeitschr. f. wiss. Photogr. 11, 381 (1912).

thereby found figures which vary from some per mille up to 100 per cent (for the carbonic-acid-assimilation). In these calculations the total augmentation of energy has most frequently been employed, but — as shown by WEIGERT — it would have been more correct to reckon with the increase in free energy, the work effected by the radiation being only computable thereby. In consequence of the above reasoning, this way of calculation can only be of technical and not of special photochemical interest, as it includes the alteration of energy in the secondary process which — for the same primary process, hence the same effect of the absorbed radiation — may involve highly different displacements of energy.

The calculations made according to the same principle on irreversible processes possess still slighter direct significance. The question here not being of accumulation, either of total or free energy, we have had to restrict ourselves to putting the absorbed amount of energy in relation to the transformation of substance produced thereby, or to the loss in total or free energy corresponding to this transformation. Thus WARBURG¹ in a series of papers has determined the "specific photochemical effect", by which he understands the quantity of gr. molecules transformed per absorbed calory. It will be shown below how this quantity on certain conditions may be of unsuspected importance.

It is evident from the above explanation that the more insight we get into the character of the primary photochemical process, the more exactly shall we be able to determine the efficiency of the absorbed radiation. Among

¹ Sitzungsber. d. Berliner-Akad. 1911, 746. 1912, 216. 1913, 644. 1914, 872. 1915, 230. 1916, 314. 1918, 300.

the manifold hypotheses put forth to this end, only a single one has hitherto been applicable as a foundation for quantitative calculation. This hypothesis takes it for granted that the primary photochemical effect consists in a split off of electrons produced by the effect of resonance from the absorbed radiation, the frequency of which must fairly coincide with the "characteristic vibration" of the electron. The quantitative forming of this view is due to EINSTEIN¹, who in 1905 advanced his "photochemical law of equivalence", according to which, in simple cases, each absorbed quantum can liberate 1 electron. If the said process be of so simple a nature as to enable us to judge of the magnitude of the transformation which will be the result of the split off of 1 electron, then we have here a possibility of calculating beforehand the total chemical effect of a certain absorption, when the wave-length, and with it the magnitude of the quantum, is known. This calculation WARBURG has tried to carry through in the above mentioned series of papers, whereby he found good accordance with the experiments in some cases and not in others. But it is to be remembered, that everyone of these kind of calculations requires a special hypothesis of the mechanism of the said process.

Without knowing EINSTEIN's work I tried in 1912² to compare the absorbed amounts of light with the amounts of energy which according to the quantum-theory are — for a series of light-processes — necessary for the split off of an amount of electrons, corresponding to the observed transformation of substance. By means of the information at hand in the literature I attained to a system of the

¹ Ann. d. Physik (4) 17, 148 (1905). 37, 832 (1912).

² Zeitschr. f. wiss. Phot. 11, 92 (1912).

photochemical processes founded on energetic basis. Others¹ have later made similar measurements and calculations, and in 1913 BODENSTEIN² on the same basis, but without knowing my work, has set forth a detailed theory of the nature of the photochemical effect. All these works have shown that, as a rule, there is no simple relation between the absorbed energy and the one required by the quantum-theory, the latter being very frequently far greater than the former.

The assumption, that the primary photochemical process consists in a split off of electrons, has naturally given rise to a series of attempts to demonstrate these liberated electrons, which result in a demonstration of light-electrical sensitiveness (Hallwachs-Effect) in the primary sensitive substance. All these experiments³ gave a negative result. This, in connection with the fact that the absorbed amounts of energy in many cases are too small to explain the necessary split off of electrons, must — according to my opinion — cause us to disregard this explanation, at any rate as a general theory. By the atom-model made by N. BOHR⁴, according to which the Planck-effect-quantum $h\nu$ no longer corresponds to the complete split off of electrons, but only to the moving of these from one stationary state to another, we should presumably get

¹ HENRI and WURMSER, *Compt. rend.* 156, 1012 (1913). 157, 126 (1913). BOLL, *Compt. rend.* 156, 1891 (1913). *L'évolution photochimique des électrolytes*, Paris 1914.

² *Zeitschr. f. physikal. Chemie* 85, 329 (1913).

³ KUMMEL, *Zeitschr. f. Elektroch.* 17, 409 (1911), LUDLAM, *Philos. Mag.* (6), 23, 757 (1912), LENARD and RAMSAUER, *Sitzungsber. Heidelb. Akad.* 1910, Nr. 28, 31, 32, 1911, Nr. 16, 24. VOLMER, *Ann. d. Phys.* (4) 40, 775 (1913). LE BLANC and VOLMER, *Zeitschr. f. Elektroch.* 20, 494 (1914).

⁴ *Phil. Mag.* (6), 25, 10 (1913).

over the difficulty which lies in the lacking light-electrical sensitiveness in the primary sensitive substances. But the other difficulty, that the absorbed amounts of energy are too small for the moving of the electrons to an exterior stationary condition, nevertheless remains.

On the other hand it looks as if — starting from quite another consideration — a quantitative accordance between the absorbed and the necessary amounts of energy can be demonstrated. As has first been pointed out by ARRHENIUS¹, a reaction with measurable velocity can only be imagined possible if a certain, slight fraction of the molecules at hand at each single moment are in such a state that they are able to react, hence, are active. If they were all in the same state, they would be obliged, either to react all at the same time, or not at all. The velocity of reaction under given circumstances must according to this conception be a measure for the fraction of all of the molecules in the active state. I have previously² applied this view for an explanation of the optical sensitisation. In accordance with this, the effect of the sensitiser should consist in transforming the absorbed radiation in such a way, as to render the energy gained thereby able to give some of the other molecules present that accretion of energy which would make them active, “help them over the top”.

R. MARCELIN³ has already in 1914, however, been able to convert these purely qualitative considerations into quantitative calculations.

MARCELIN compares the distribution of energy for a

¹ Bihang till kgl. Svenska Vet. Akad. Handl. 8, No. 13, 14 (1884).

² Forh. 16. skand. Naturforskerm. 1916, 279.

³ Ann. de physique 3, 120 (1914).

large amount of molecules with a swarm of bees gathering around the queen. The swarm is densest towards the centre and decreases in density outward, the distribution being thus determined by the MAXWELL-BOLTZMANN-GIBBS-distribution-law. If now we imagine a surface of a sphere at a great distance from the centre, then in each single moment only quite a few of the bees will pass this surface from within and outward. If now these bees be supposed to be removed as soon as they pass the surface of the sphere from within, then, next moment, they will be replaced by others, which are also removed, and so on, and the whole phenomenon then gives the picture of a slowly occurring process. This sphere-surface represents a certain content of energy per gr. molecule, which MARCELIN calls the "critical energy", and the bees which reach the surface correspond to the active molecules, the peculiarity of which above all others is, hence, that they possess just this critical energy. The critical energy is assumed — in a given system — to be independent of the temperature, and it is assumed that all active molecules actually react. By consideration of the influence of the temperature upon the reaction-velocity MARCELIN has succeeded in finding the difference between the critical energy and the mean-energy of the molecules, hence, the average accretion of energy which will be necessary to render all inactive molecules able to react. This "relative critical energy", E_k , is, according to MARCELIN, for one gr. molecule equal to:

$$E_k = RT^2 \frac{d \ln k}{dT}$$

where R is the gas constant, T the absolute temperature and k the velocity-constant for the said process.

If now the process be light-sensitive it will be of considerable interest to compare the necessary accretion of energy E_k with the amount of the absorbed light-energy which is required in order to produce a certain reaction-velocity. I have executed this comparison partly for my own measurements of the oxidation of the hydrogen iodide, and partly in a couple of cases occurring in the literature which offered the necessary data. In the tables are besides denoted the amounts of energy, $nNh\nu$, which would be necessary if the primary process consisted in a split off of electrons or in a moving of these from one stationary state to another.

I. Own Measurements.

The Oxidation of the Hydrogeniodide.

The temperature-coefficient for the dark-process according to PLOTNIKOW¹ is 2,07². Hence:

$$E_k = 83,15 \cdot 10^6 \frac{293 \cdot 303}{10} \ln 2,07 = 53,7 \cdot 10^{10} \text{ Erg.}$$

Table 1.

Wave-length	transformed mol. per sec. in 5 mm ³ = n	nE_k	absorbed energy	$nNh\nu$
	Experiments with passage of air.			
436 $\mu\mu$	0,75 · 10 ⁻¹¹	4,0 Erg.	5,9 Erg.	21,0 Erg.
—	1,00 >	5,4 >	6,5 >	28,0 >
405	0,59 >	3,2 >	2,9 >	17,7 >
—	0,50 >	2,7 >	2,3 >	15,0 >
366	0,68 >	3,7 >	5,5 >	22,6 >
—	0,52 >	2,8 >	3,5 >	17,3 >

¹ Zeitschr. f. physikal. Chemie 64, 215 (1908).

² In an earlier paper (Zeitschr. f. physikal. Chemie 58, 214 (1907) the same author had determined the temperature-coefficient at 2,86, which would render all of the E_k -values in the table somewhat greater, hence render them still more conformable.

Wave-length	transformed mol. per sec. in 10 mm ³ = <i>n</i>	<i>nE_k</i>	absorbed energy	<i>nNhν</i>
313 μμ	1,33 · 10 ⁻¹¹	7,2 Erg.	3,1 Erg.	51,8 Erg.
—	1,50 >	8,1 >	3,5 >	58,4 >
Experiments with passage of oxygen.				
	transformed mol. per sec. in 5 mm ³ = <i>n</i>			
366	150 · 10 ⁻¹¹	8,1 >	3,7 >	50,0 >

II. Other Measurements.

The Decomposition of the Hydrogen iodide

The temperature-coefficient is according to BODENSTEIN¹:

$$\ln k = \div \frac{21922,5}{T} \div 14,468 \ln T + 0,023055 T \div 104,185.$$

Photochemical decomposition and measurement of energy: WARBURG². The calculation is applied to experiment No. 19, where the transformation is greatest:

Wavelength	<i>n</i>	<i>nE_k</i>	<i>E_{abs}</i>	<i>nNhν</i>
282 μμ	8,25 · 10 ⁻⁶	1,36 · 10 ⁷	1,64 · 10 ⁷	3,45 · 10 ⁷ Erg.

The Decomposition of the Peroxide.

The temperature-coefficient for the platinum catalysis according to BREDIG and M. v. BERNECK³

$$\ln \frac{k_1}{k_2} = 5899 \frac{T_1 - T_2}{T_1 T_2}$$

Photochemical decomposition and measurement of energy: HENRI and WURMSER⁴

Wavelength	<i>n</i>	<i>nE_k</i>	<i>E_{abs}</i>	<i>nNhν</i>
280 μμ	1	0,82 · 10 ⁻¹²	1,54 · 10 ⁻¹²	6,7 · 10 ⁻¹² Erg.

¹ Zeitschr. f. physikal. Chemie 29, 306 (1899).

² Sitzungsber. d. Berliner-Akad. 1918, 300.

³ Zeitschr. f. physikal. Chemie 31, 329 (1899).

⁴ Compt. rend. 157, 126 (1913).

The temperature-coefficient will undoubtedly be far greater for the peroxide-decomposition itself (without platinum) which — as known — only has a measurable velocity at high temperature, than for the platinum catalysis¹. Putting $nE_k = E_{\text{abs}} = 1,54 \cdot 10^{-12}$, we find the temperature-coefficient equal to 3,52, (instead of 1,7 for the platinum catalysis), which is a far more probable value.

Even if the material is, for the present, very limited², all the evidence seems to suggest that the relative critical energy is equal to the absorbed energy, that the latter consequently is completely utilised, as it brings all of the absorbing molecules into an active state, i. e. a state capable of reacting. The deviations which are found, and which almost all tend towards the relatively critical energy being a little smaller than the absorbed, are explained by defective stirring. As far as can be seen from the description of experiments, stirring was not employed at all in WARBURG'S experiments, beyond the movement produced by slow passing-through of hydrogeniodide, and, the absorption being strong (70 per cent), and the bundle of rays only having been $\frac{1}{6}$ of the transverse section of the cell, the radiation cannot have been capable of exerting its full effect. WARBURG'S measurements show also that nE_k decreases with decreasing wave-length, i. e. with increasing absorption.

Quite the same thing holds also for VRANEK'S measurements of the decomposition of the potassium kobaltioxalate.

¹ NERNST (*Zeitschr. f. Elektroch.* 11, 710 (1905)) has for the decomposition of the pure peroxide found the temperature-coefficient 1,32 between 270 and 336°. But it is possible, partly that the process also under these circumstances is catalytic (the effect of the walls), and partly we cannot compute from this the magnitude of the coefficient at ordinary temperature.

² More accurate experiments are being prepared.

Table 2.

n	E_k	$n \cdot E_k$	Wavelength	E_{abs}	Extinction
0,0002	$1,12 \cdot 10^{12}$	$2,24 \cdot 10^8$	436 μ	$7,6 \cdot 10^8$ Erg.	180,4
>	>	>	405 μ	5,8 >	163,5
>	>	>	366 μ	4,3 >	58,5

For my experiments with the oxidation of the hydrogen-iodide the same holds good. Despite a very vigorous stirring I am not certain of having obtained the complete utilisation of the absorbed energy, (the absorption was in every place complete), the process occurring very rapidly. If we, f. inst. by making the distance to the lamp greater, were to decrease the velocity and thereby make the stirring more effective, the energy-measurement would simultaneously become so incorrect that hardly anything would be gained by this.

Other apparent deviations from the found regularity will be dealt with in a later section.

We may now achieve a corroboration of the correctness of the found law from a series of other measurements, not computable in the same way as those above, the temperature-coefficient not being known.

Taking it for granted that the temperature-coefficient $k_{t+10} : k_t$, which for processes with conveniently measurable velocity as a rule lies between 2 and 4, may rise to 10, when the process is considered at a far lower temperature than that at which its velocity is measurable¹, we may from the found law of critical efficiency compute the limits for the "specific photochemical effect", as it is defined by WARBURG. This "specific photochemical effect" Φ

¹ For ferric oxalate, the decomposition of which is not measurable until above 40°, we compute from LEMOINE'S measurements (Ann. chim. phys. (6), 30, 289 (1893)) for 15–25° a temperature-coefficient of 8,5. For the decomposition of hydrogen chloride VAN'T HOFF computes 17,2 (Vorles. üb. theoret. u. physik. Chemie I, 231).

is the transformed amount of substance per calorie of the energy absorbed.

Hence:

$$\Phi = \frac{n}{E_{\text{abs}}}$$

As, according to the law of critical efficiency, $nE_k = E_{\text{abs}}$,

$$\Phi = \frac{1}{E_k}$$

From MARCELIN'S formula is computed, for the temperature-coefficient 2, $\Phi = 8,1 \cdot 10^{-5}$, for the temperature-coefficient 10, $\Phi = 2,4 \cdot 10^{-5}$.

The following examples are found in the literature:

Table 3.

Process	Wavelength	$\Phi \cdot 10^5$	Examined by:
$\text{NH}_3 \rightarrow \text{N} + 3 \text{H}$	209 $\mu\mu$	0,172	WARBURG ¹
$\text{O}_2 \rightarrow \text{O}_3$	253 "	0,98	"
"	209 "	1,35	"
$\text{O}_3 \rightarrow \text{O}_2$	287 "	2,96—6,70	"
"	253 "	0,25—7,08	"
"	209 "	6,58—8,09	"
$\text{HBr} \rightarrow \text{H} + \text{Br}$	253 "	1,79	"
"	209 "	1,53	"
$\text{HJ} \rightarrow \text{H} + \text{J}$	282 "	2,09	"
"	253 "	1,85	"
"	209 "	1,44	"
Nitrobenzaldehyde \rightarrow Nitrosobenzoic acid	405 "	ca. 2	KUMMERER ²
"	366 "	ca. 4	"

That many of these figures are smaller than the denoted lowest limit, cannot give rise to any astonishment. The reason may partly be the above, that a complete utilisation of the absorbed energy can only be expected when working in thin layers and with a stirring so vigorous, that the velocity of the light-process is very

¹ Sitzungsber. d. Berliner-Akad. 1911—18.

² Inang.-Dissert. Berlin 1914.

slight when compared with the equalisation of the concentration-difference produced by the stirring, and partly the deviations may arise from the fact, that the temperature-coefficient of the process after all is higher than the highest assumed limit.

Above all it must be borne in mind that nothing whatever can be stated beforehand in any other way about the magnitude of the specific photochemical effect, and that the values might consequently be imagined to be spread over a very large interval, while they actually lie within fairly narrow limits, a circumstance which may be naturally explained by the fact that the temperature-coefficients, too, only vary comparatively little.

From WARBURG's measurements we may deduce yet another corroboration of the law of critical efficiency. The reversible darkness-process:



is supposed to be displaced to the right by heating, which means that the process $A \rightarrow B$ has a greater temperature-coefficient than the opposite process. It follows, consequently, that the process $A \rightarrow B$ must also have a greater relative critical energy, hence, a smaller specific photochemical effect than the process $B \rightarrow A$. By consideration of table 3 it is seen in accordance herewith that Φ for all wavelengths is smaller for the process $O_2 \rightarrow O_3$ than for the reverse, which agrees with the fact that the equilibrium by heating is displaced in favour of the formation of ozone.

II. Consequences of the Law of Critical Efficiency.

If the here found law of critical efficiency is corroborated on closer examination, it will firstly yield a highly

welcome means for independent determination of the relative critical energy, a quantity which will undoubtedly in future play a very great rôle in the further development of general chemistry.

Secondly, it evidently means a great step towards a quantitative control of the photochemical processes, as, for the first time, the possibility is here present that — independent of all hypotheses of the special mechanism of the primary reaction — we may beforehand calculate the light-sensitiveness of the process, if only the temperature-coefficient of the corresponding darkness-reaction be known.

Furthermore the law of critical efficiency throws light on various photochemical relations which have hitherto not been explainable, thus f. inst. the smallness of the temperature-coefficients. The temperature-coefficient of the dark-processes may in its dependency on the temperature most frequently be expressed by an equation such as:

$$\ln k = \frac{A}{T} + B \ln T + CT + D,$$

where B , C and D are far smaller than A . By differentiation we obtain:

$$\frac{d \ln k}{dT} = \frac{A}{T^2} + \frac{B}{T} + C.$$

Now:

$$E_k = RT^2 \frac{d \ln k}{dT}.$$

If in the first approximation we put B and C equal to zero, we obtain for two different temperatures:

$$\frac{E'_k}{E_k} = \frac{\Phi}{\Phi'} = \frac{T^2}{T_1^2} \cdot \frac{T_1^2}{T^2} = 1.$$

$\Phi' : \Phi$ is the temperature-coefficient of the light-process, which will accordingly be 1 or — when all the terms in the formula for lnk are included — at any rate very close to 1. Now it has long been known¹ that temperature-coefficients for photochemical processes are generally far lower than for the dark-processes, and in many cases approach very closely to 1.

We also, however, know several light-processes, with temperature-coefficients around 1,2 and 1,4, and even a very few between 2 and 4, which would require a quite absurdly big alteration of the temperature-coefficient of the dark-process with the temperature. Now it must be remembered that all of these temperature-coefficients are computed for the same incident amount of light, not for the same absorbed amount of light. But in the above argument I have taken it for granted that E_{abs} was uniform in the two considered temperatures which need not be the case at all. If this is not the case, we have at two temperatures:

$$\begin{aligned} n_1 E_k &= E_{\text{abs}} \\ n_2 E'_k &= E'_{\text{abs}}. \end{aligned}$$

The temperature-coefficient $n_1 : n_2$ is then

$$\frac{n_1}{n_2} = \frac{E_{\text{abs}} \cdot E'_k}{E'_{\text{abs}} \cdot E_k}$$

In order to reach the temperature-coefficients usually given, we must consequently divide the fraction $E'_k : E_k$ by the ratio between the amounts of light which are absorbed at the two temperatures in question, and the more this ratio deviates from 1 the more the temperature-coefficient will also deviate from 1.

¹ E. GOLDBERG, Zeitschr. f. wiss. Photogr. 4, 103 (1906).

Another peculiar circumstance with regard to the photochemical temperature-coefficient is also explained by the law of critical efficiency. In several recent works PADOA and his co-workers¹ have shown for a series of photochemical processes, that the temperature-coefficient for a single process most frequently increases with the wavelength. The examined processes are:

Table 4.

Light-sensitive system	Temperature-coefficient			
	Green	Blue	Violet	Ultra-violet
Chlorine-hydrogen mixture	1,50	1,31	1,21	1,17
EDER's liquid	1,75	1,21	—	1,05
Benzaldehydephenylhydrazone	—	1,08	1,04	—
Triphenylfulgide (coloration)	1,67	1,29	—	—
Salicyliden- β -naphthylamine	1,80	1,45	1,39	—
		Red	Yellow	
Triphenylfulgide (de-coloration)	1,08	0,89	—	—

On the other hand 1,05 was found independent of the colour for photographic plates.

Now it is a fact that, by heating the absorption-curve is most frequently displaced towards the long-waved end of the spectrum. This must involve that the relation $E_{\text{abs}} : E'_{\text{abs}}$ must increase the more we move from the absorption-maximum towards the long-waved end of the spectrum, whereas it must decrease when we move the opposite way. As according to the above, it is materially this circumstance which determines the magnitude of the photochemical temperature-coefficient, it is intelligible that it varies with the wave-length and just in the way shown by the observations. For chlorine-hydrogen mixture, EDER's liquid, benzaldehydephenylhydrazone and salicyliden- β -naphthylamine the absorption-maximum everywhere lies in

¹ Atti d. Reale Accad. d. Lincei (5) 22 II 500 (1913). 24 I 828 (1915). 24 II 97 (1915). 25 I 808 (1916). 25 II 168, 215 (1916).

ultraviolet. The temperature-coefficient must accordingly either keep independent of the wave-length — if the absorption is independent of the temperature — or rise towards green. Triphenylfulgide has its absorption-maximum in blue-violet, and must consequently behave in the same manner. The (phototropic) triphenylfulgide, coloured by the insolation is, on the contrary, blue, consequently has absorption-maximum in orange. Towards red on the long-waved side of the maximum, the temperature-coefficient must then rise above 1, towards yellow, on the short-waved side of the maximum it must, on the contrary, fall below 1, as is also shown by the observations.

Also the possibility of chemi-luminescence may be elucidated from the law of critical efficiency. According to MARCELIN¹ the critical energy is uniform for the two opposite processes in a reversible process. If the mean-energies for the two processes are E_1 and E_2 , the relative critical energies E_k and E'_k , then consequently:

$$E_1 + E_k = E_2 + E'_k.$$

The energy yielded after the electron has “passed the top”, E'_k , must presumably be yielded in quanta, the frequency of which is computable according to the formula:

$$E'_k = Nh\nu$$

where N is the figure of AVOGADRO, h PLANCK'S constant and ν the frequency. As a resource in the calculation of E'_k in those cases where it cannot be directly measured (or is not known), we make use of the circumstance, that the difference between E_k and E'_k is equal to the reaction-heat in the said process. In this way I have in the table

¹ Ann. de physique 3, 173 (1914).

below computed E_k firstly for the process $O_3 \rightarrow O_2$ starting from the specific photochemical effect for the opposite process, which is assumed to be correct. Hereby we obtain the value $2,7 \cdot 10^{-5}$ for Φ , which is more probable than WARBURG's experimentally found value $1,35 \cdot 10^{-5}$, which, as earlier mentioned, is undoubtedly too low on account of the lack of stirring. Furthermore for several other processes where E_k and the reaction-heat is known. The reaction-heat Q as well as the other energy-quantities are expressed in erg.

Table 5.

Process	$E_k \cdot 10^{-10}$	$Q \cdot 10^{-10}$	$E'_k \cdot 10^{-10}$	$\nu \cdot 10^{-14}$	Wavelength
$O_2 \rightarrow O_3$	155	$\div 95$	60	1,52	1970 $\mu\mu$
$O_3 \rightarrow O_2$	60	$+ 95$	155	3,93	764 >
$2 HJ + O \rightarrow J_2 + H_2O$	53,7	$+ 30,8$	84,5	2,15	1390 >
$HJ \rightarrow H + J$	200	$+ 12,6$	212,6	5,4	557 >
$H + J \rightarrow HJ$	212,6	$\div 12,6$	200	5,1	592 >
$HBr \rightarrow H + Br$	234	$\div 50,6$	183,4	4,7	642 >
$H + Br \rightarrow HBr$	183,4	$+ 50,6$	234	6,0	503 >
$NH_3 \rightarrow N + 3 H$	2430	$\div 50$	2380	60	50 >
$N + 3 H \rightarrow NH_3$	2380	$+ 50$	2430	62	48 >

This calculation is of course only of interest on the assumption that the measured reaction-heat correspond to the simple reaction scheme which is given in the table, E'_k thus being rendered without any break, without division processes. On this assumption the table shows that the decomposition and formation both of the hydrobromic acid and the hydriodic acid, as far as these processes could be made to occur rapidly in darkness at ordinary temperature, must have a possibility of luminescing in green-orange, and the transformation ozone \rightarrow oxygen in red. The transformation oxygen \rightarrow ozone and the oxidation of the hydriodic acid, on the contrary, emits

ultra-red radiation, and the decomposition and formation of ammonia emits ultra-violet radiation in the not so easily accessible domain below $200 \mu\mu$. About all these processes it holds true, however, that at present we do not know any means to increase their reaction-velocity at ordinary temperature to such a degree that there can be any possibility of demonstrating or measuring this secondary radiation. Several of them even represent displacements of equilibria, which cannot be made at all without external supply of energy. The calculation is only carried through in order to show, how a luminescent system (f. inst. pyrogallol in alkaline liquid + an oxidizing substance or another of the numerous chemi-luminescent processes) should be investigable, if we start from the view here maintained. Furthermore the result has the interest of showing that the found frequencies after all lie within the region with which we can on the whole reckon when the question is of radiation from atoms and electrons.

III. Deviations from the Law of Critical Efficiency.

A regularity like the photochemical law of critical efficiency, which is at least made probable by the experiments and considerations which have been described in the foregoing sections, must — according to its nature — be assumed to be generally valid, in the same way as, f. inst. the law which describes the distribution of a substance between two phases. But just as the last named law in many cases seems to be invalid by the fact that the substance in one phase may be found in several different conditions or compounds, while the law only reckons with the same kind of molecules in both phases, thus it

might also be expected beforehand that many apparent deviations from the photochemical law of critical efficiency may be found. In the following I will go through some of the causes of the deviations which can be recognized for the present. It will be natural to divide these into positive and negative deviations.

The positive deviations, by which the measured light-sensitiveness is greater than the computed, may as a rule be caused by the primary formation of a catalyst. We can here as little as in the darkness-catalyses indicate anything beforehand as to how much such a catalyst is able to accelerate the process or how great the "induction-factor" is, in so far as the catalyst itself is consumed in the course of the process. Consequently no limit can be given for the total light sensitiveness, which can be obtained, when a very active catalyst is formed in the primary process.

A typical example of this kind we have in the catalysis of the peroxide with potassium-ferro-cyanide¹. Under the circumstances applied in this investigation (left for 30 minutes) the induction-factor has the following values:

Table 6.

$c_{H_2O_2}$	λ	$E_k \cdot 10^{-5}$	$E_{abs} \cdot 10^{-4}$	$E_k : E_{abs}$
0,04-m	405	3,3	0,73	45
"	"	3,3	0,70	48
"	366	39	9,8	40
"	"	54	10,0	54
"	"	72	10,7	67
"	"	113	21,3	53
				51
0,02-m	"	64	17,2	37
"	"	152	38,6	39
				38

¹ Kgl. Danske Vid. Selsk. Math.-fys. Medd. II. 1.

The light-catalyst here being exceedingly constant, we should obtain a far higher induction-factor by leaving the mixture in the dark for a longer period. In experiment 13 (*loc. cit.*) we have, *f. inst.* by leaving for $2\frac{1}{2}$ hours, the induction-factor 270, when the decomposition in the dark is subtracted.

Quite an analogous case is offered by the photographic plate. The latent image, at the formation of which the law of critical efficiency might undoubtedly be applicable, here represents the light catalyst. It is at least as constant as the catalyst formed by exposure of potassium-ferrocyanide, and the total process has (by the development) a very high induction-factor. How great it is, is not known, the few quantitative determinations of the light-sensitiveness at hand only referring to the incident and not to the absorbed light.

To the same group probably also belongs the reaction in chlorine-hydrogen mixture which, from its discovery, has been reckoned as one of the most sensitive of all known photolyses. BODENSTEIN¹ computes the quantum sensitiveness at 10^6 , but an actual determination of the sensitiveness has never been carried out.

While the positive deviations from the law of critical efficiency can no doubt mainly be explained from this point of view² the negative deviations may originate from various sources. We have previously (*v. p.* 16) mentioned a purely technical cause, the lack of stirring. A frequently occurring case is, that besides the actual light-sensitive substance another, very absorbing, substance is found. The

¹ *Zeitschr. f. physikal. Chemie* 85. 346 (1913).

² Provided, that it is quite the same process, which is measured in darkness and in light.

measured absorption will then only partly be of any good to the actual sensitive substance. As an example may be named the oxidation of the quinine with chromic acid, where LUTHER and SHANNON FORBES¹ have succeeded in finding the part of absorbed light-energy which belong to the quinine, which is here the sensitive substance. Unfortunately the two investigators have not measured this absorption in absolute measure, and the dark-temperature-coefficient of the process is not known either, as far as we know, for which reason the calculation cannot be carried through.

If the non-sensitive, absorbing substance be formed by the sensitive substance, the concentration of the latter is decreased to a frequently unknown degree. The sensitiveness calculated for the total amount of this substance will then always be far smaller than the actual sensitiveness.

While these examples deal with injurious absorption of the incident, active light, it might also be imagined, that the secondary radiation, to which — according to a hypothesis advanced in another paper — the absorbed radiation in many cases is transformed, was absorbed by other substances than that upon which it was actually to act. Deviations, which perhaps may be explained in this way, is found in WARBURG'S works.

While the specific photochemical effect of the decomposition of the hydriodic acid and the hydrobromic acid is independent of the concentration of these substances, hence, is constant, WARBURG² finds highly peculiar circumstances in the photochemical des-ozonisation (Table 7).

The specific photochemical effect which, according to

¹ Journ. amer. chem. Soc. **31**, 770 (1909).

² Sitzungsber. der Berliner Akad. **1913**, 644.

Table 7.

Ozone, solved in:	Wave- length	Ozone- Concentration	Absorption of the Ozone	$\Phi \cdot 10^5$
Oxygen	253	9,29 —0,75	1 —0,94	3,13 —0,44
>	>	0,47 —0,18	0,752—0,288	0,253
Nitrogen	>	2,56 —0,65	0,98 —0,88	2,37 —0,99
>	>	0,65 —0,167	0,877—0,267	0,97
Helium	>	0,429—0,361	0,804—0,710	1,60 —1,44
Oxygen (moist.)	>	8,49 —0,91	1	7,08 —1,84
>	>	10,50 —0,80	1 —0,86	4,23 —1,49
>	209	8,49 —5,66	0,857—0,733	8,09 —6,58
>	287	8,15 —6,27	0,96 —0,92	6,70 —2,96

the law of critical efficiency should be constant, thus varies very much, both with the concentration of the ozone and the nature of the solvent.

Let us, f. inst. consider the mixture of ozone and oxygen. By exposure to 253 $\mu\mu$ only the ozone absorbs to a mentionable degree so that nothing could be lost in this way. Now WEIGERT¹ has made it probable, that a light catalyst is formed by the photochemical desozonisation. According to the radiation-hypothesis this catalyst acts by transforming the absorbed radiation quantitatively to a far shorter wave-length, which may also be absorbed by the ozone. Just as iodine-ion and tri-iodine-ion, the leuco-compounds and the corresponding colour-substances possess a common absorption-region in ultra-violet², we may be allowed to consider it probable that the oxygen, too, has the same absorption-region in furthest ultra-violet, as its oxidation product ozone. This means that the oxygen consumes part of the secondary radiation which was to be employed for the desozonisation.

The experiments now show, firstly, that the specific

¹ Zeitschr. f. physikal. Chemie **80**, 78 (1912).

² Kgl. Danske Vid. Selsk. Math.-fys. Medd. II. 2.

photochemical effect for the same ozone concentration is higher when ozone is mixed with nitrogen, than when mixed with oxygen, and still higher, when mixed with helium. According to our knowledge of the absorption in furthest ultra-violet¹ of these three gases, we seem justified in supposing that oxygen has the greatest, helium the smallest extinction of the three. The secondary radiation of the ozone might therefore be best utilised for decomposition of ozone when the surrounding molecules consist of helium, not so well when the ozone is diluted with nitrogen and least when mixed with oxygen, as also shown by the experiments.

In very small ozone-concentrations WARBURG finds for the mixture with oxygen and nitrogen, that the specific photochemical effect becomes fairly constant, even if the ozone-concentration, and with it the absorption, vary. This constancy arises by compensation of two inverse influences.

According to WARBURG's statement, the radiation passed through a 0,95 cm. high and 0,43 wide split into the circular cell, the diameter of which was 1,7 cm and the thickness 1,9 cm. and spread somewhat there. When no stirring is employed only a fraction of the contents of the cell would consequently be able to be exposed during the 4 minutes each experiment lasted. But the measured loss of ozone corresponds to all of the contents of the cell, hence, is smaller than the loss of ozone in the exposed part of the cell. The smaller the ozone-concentration is the greater is the exposed part of the cell — on account of the decreasing absorption — the greater, consequently

¹ LYMAN: "The Spectroscopy of the Extreme Ultra-Violet", p. 63, 69 (1914).

also the measured specific photochemical effect in proportion to the correct effect. This augmentation of Φ with decreasing ozone-concentration is, however, counteracted by the loss described above by the absorption of the solvent of the secondary radiation, and it is at any rate possible that the combination of these two opposite influences can produce the approximate constancy, which has been found by WARBURG.

Suppose v to be the volume of the cell, v_1 the highly exposed, and v_2 the slightly exposed and dark portion of the cell. The total ozone-concentration is c , the loss of concentration in the exposed part c_1 , and the measured loss of concentration c_2 . We then have:

$$cv_2 + (c \div c_1)v_1 = (c \div c_2)v,$$

from which:

$$c_2 = c_1 \frac{v_1}{v}, \text{ since } v = v_1 + v_2.$$

As mentioned v_1 is, however, not constant, but increases with decreasing absorption. The constancy of Φ occurring when the absorption is abt. 0,9, the highly exposed volume may suitably be put proportional to the thickness of layer x , which at different concentrations just brings about this absorption. If α be the extinction-coefficient we have:

$$1 \div 10^{\div \alpha c x} = 0,9, \text{ then } x = \frac{1}{\alpha c} \text{ and } v_1 = \frac{k_1}{\alpha c}.$$

The specific photochemical effect which was actually to be measured, is now pro primo the transformed amount of substance per absorbed unit of energy:

$$\frac{c_1}{I_0 (1 \div 10^{\div \alpha c})}$$

where I_0 is the intensity of the incident radiation. By the made measurement c_2 is, however, introduced instead of c_1 . Pro secundo the specific photochemical effect is furthermore decreased by the solvent's absorption of the secondary radiation, the measured specific photochemical effect Φ_2 thus being:

$$\Phi_2 = \frac{c_2}{I_0 (1 \div 10^{\div ac})} \cdot \frac{\alpha_1 c}{(\alpha_1 c + \alpha_2 (100 \div c))}$$

where α_1 and α_2 are the extinction-coefficients of the ozone and oxygen respectively for the secondary radiation.

In small ozone-concentrations the absorption — as shown by WARBURG — is very near being proportional to the concentration, therefore the quantity $1 \div 10^{\div ac}$ may be replaced by ac . Secondly the term $\alpha_1 c$ becomes very small in comparison with $\alpha_2 (100 \div c)$ and c very small in comparison with 100. By introducing the values for c_2 and v_1 the expression will consequently be:

$$\Phi_2 = \frac{c_1 k_1 \alpha_1 c}{I_0 \alpha c v \alpha c \alpha_2 100} = K_1 \frac{c_1}{c}$$

The specific photochemical effect, which was actually to be measured, is — when all disturbing influences are imagined to be removed —:

$$\Phi_1 = \frac{c_1}{I_0 (1 \div 10^{\div ac})}$$

or for small concentrations:

$$\Phi_1 = \frac{c_1}{I_0 \alpha c} = K_2 \frac{c_1}{c}$$

According to the law of critical efficiency this quantity only depends upon the temperature-coefficient of the darkness-process, hence it is constant, and Φ_2 being propor-

tional to the ideal Φ_1 , Φ_2 must be constant, as found by WARBURG, and possess the value:

$$\Phi_2 = \frac{k_1 \Phi_1 \alpha_1}{v \alpha \alpha_2 100}.$$

The difference between the measured specific photochemical effects in the mixtures with oxygen, nitrogen and helium then only depend upon the different value of α_2 . If for oxygen (see below) it be put equal to α_1 , then it will be for:

$$\text{Nitrogen: } \alpha_2 = \alpha_1 : \frac{0,97}{0,213} = \frac{\alpha_1}{3,8}$$

$$\text{Helium: } \alpha_2 = \alpha_1 : \frac{1,52}{0,253} = \frac{\alpha_1}{6,0}$$

by which helium absorbs the secondary radiation 6 times, nitrogen 3,8 times less than oxygen (and ozone).

Also in somewhat greater concentrations Φ_2 must be fairly constant as long as α is so, and the diffusion does not play any part. If we put:

$$\frac{c_1}{I_0(1 \div 10^{\div ac})} = \Phi_1$$

in the expression of Φ_2 :

$$\Phi_2 = \frac{c_1 k_1}{v \alpha c I_0 (1 \div 10^{\div ac})} \frac{\alpha_1 c}{(\alpha_1 c + \alpha_2 (100 \div c))}$$

we have:

$$\Phi_2 = \frac{k_1 \Phi_1 \alpha_1}{v \alpha (\alpha_1 c + \alpha_2 (100 \div c))}.$$

As long as c only amounts to a few per cent, and α_1 is not very large when compared with α_2 , we shall always be able to put the expression $\alpha_1 c + \alpha_2 (100 \div c)$ equal to 100, the error only amounting, perhaps, to a few per cent, which falls quite within the error-limit in WARBURG's experiments.

The formula will accordingly be:

$$\Phi_2 = \frac{k_2}{\alpha}$$

The experiments, however, exhibit both for the mixtures with oxygen and with nitrogen a fairly high increase of Φ_2 , with the ozone-concentration. But the explanation is near at hand. Table 8 contains the data in question and besides those extinction-coefficients, α , which are computed from c and the relative absorption A .

Table 8.

Ozone and Oxygen				
c	A	α	$\Phi_2 \cdot 10^5$	$\alpha \Phi_2 \cdot 10^5$
9,29	1	—	3,13	—
2,92	0,95	0,45	1,48	0,67
1,85	0,98	0,92	0,68	0,63
0,75	0,94	1,63	0,44	0,72
0,47—0,18	0,75—0,29	1,60	0,253	0,41
Ozone and Nitrogen				
2,56	0,98	0,66	2,37	1,57
1,41	0,93	0,82	1,70	1,40
0,65	0,88	1,42	0,99	1,40
0,46—0,17	0,74—0,27	1,60	0,97	1,55

The table shows the astonishing circumstance that the extinction-coefficient decreases very much with increasing ozone-concentration. Such a deviation from BEER'S law is not unknown in the case of gases. WARBURG¹ has for oxygen found the inverse relation, that the extinction-coefficient increases more than the oxygen-pressure. If we take regard to this variation of the ozone, the table shows that the product $\alpha \Phi_2$ is constant, as demanded by the formula. With regard to the mixture with nitrogen this constancy extends over all the region, whereas at the mixture with oxygen the most diluted mixtures deviate

¹ Sitzungsber. d. Berliner-Akad. 1915, 230.

pretty much from the others, without the reason for this being discoverable from the description of the experiments.

If we rise to still greater concentrations there are two cases to consider; the expression $\alpha_1 c + \alpha_2 (100 \div c)$ cannot anymore be put constant, and the diffusion here begins to operate. WARBURG's measurements of greater ozone-concentrations now only comprise mixtures with oxygen, where there might be reason to assume that α_1 and α_2 are fairly uniform. COEHN and STUCKHARDT¹, for the analogous pair of substances iodine-hydrogeniodide have found that the two substances not only possess approximately the same absorption-region for ultra-violet, but also nearly the same extinction. In the same way it must be allowable to assume in the first approximation, that the oxygen has the same absorption-region and extinction in furthest ultra-violet, as its oxydation-product, the ozone. Thereby the fraction will be:

$$\frac{\alpha_1 c}{\alpha_1 c + \alpha_2 (100 \div c)} = \frac{c}{100}.$$

The velocity of diffusion can be put proportional to the difference in the concentration between the exposed and the non-exposed part of the cell, hence to c_1 . For this reason no other alteration in the formula for Φ_2 takes place than the introduction of a new constant. After contraction the found specific photochemical effect will be:

$$\Phi_2 = \frac{k_3}{\alpha}.$$

As shown above α decreases with increasing ozone-concentration, whereby the fairly large rise in Φ found by WARBURG in other experimental series is explained.

¹ Zeitschr. f. physikal. Chemie **91**, 722 (1916).

The values of α , denoted in table 8, are, however, too incorrect for us to determine their dependency on the concentration with any certainty, nor is it for this reason possible to put forth any certain relation between Φ and c .

Results of this work.

The classification of the photochemical processes into work-accumulating and work-yielding processes does not agree with our present knowledge of the nature of the photolyses, but is essentially of technical interest.

On comparing the energy-absorption, necessary for the oxidation of a certain amount of hydriodic acid, with the energy which according to MARCELIN'S calculation is necessary in order to render the same quantity of hydriodic-acid molecules able to react (active), it appears that these two quantities of energy are identical. The absorbed energy is, hence, quantitatively utilised in order to make the absorbing molecules able to react. This law is verified in two other processes.

This law of critical efficiency explains the peculiar circumstance that the "specific photochemical effect" (WARBURG) for a series of very different processes is of the same order of magnitude.

The law of critical efficiency renders it possible in many cases to calculate the light-sensitiveness of a process beforehand, if only its darkness-temperature-coefficient be known.

The law of critical efficiency gives a natural explanation of the circumstance that the temperature-coefficients of

the photochemical processes are generally very small and sometimes increase with the wave-length.

The law of critical efficiency elucidates the possibility of chemi-luminescence.

The law of critical efficiency gives a probable explanation of the empirically found rule, that the less sensitive a process is to a certain wave-length, the more easily accessible it is to the optical sensitising for this wave-length, and vice versa.

The deviations occurring from the law of critical efficiency may partly be explained by experimental errors, as insufficient stirring or lack of knowledge of the absorption of the actual sensitive substance, partly by the formation of a light-catalyst, and finally by the assumption, which is supported by the observations on zinc oxide (which will be published later on) and the oxidation of the hydriodic acid, that the absorbed radiation in many cases is quantitatively transformed to radiation of a far smaller wave-length. The deviations from the law of critical efficiency are then due to the fact that this secondary radiation is not only absorbed by the substance, the transformation of which is to be effected hereby, but also by other substances.

Royal Technical College of Copenhagen,

May 1919.



